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XXIII. *Statistical Equilibrium with Special Reference to the Mechanism of Ionization by Electronic Impacts.*

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§ 1. *Introduction.*

IN a number of recent papers, the earliest by Klein and Rosseland †, it has been shown that the study of specific atomic processes of energy exchange, in quite general terms, is likely to prove exceedingly fruitful. The underlying idea may be expounded as follows. The laws of thermodynamics and of statistical mechanics (modified to include the modern quantum theory) specify certain characteristics of the equilibrium conditions of matter. The former are believed to be of universal applicability, the latter hardly extend as yet much beyond the distribution laws of dilute gaseous assemblies. In their proper regions, however, we believe these laws to be of general validity, and they then form a framework to which all detailed processes of energy exchange must conform. We believe in fact that these laws are true whatever the mechanism of such processes may be. It seems quite certain that, for example, the law of distribution of the velocities of free electrons must be the same in any enclosure in thermodynamic equilibrium. Accepting it, we can consider various assemblies at the same temperature, in

* Communicated by the Author.

† Klein & Rosseland, *Zeit. für Phys.* iv. p. 46 (1921).

which different processes of exchange are going on, or the same processes at rates which can be altered relatively to one another by altering the concentrations. Since the resulting distribution laws must be the same in form, it follows that any one process of exchange acting in a particular direction must be invariably accompanied by an analogous reverse process. The pair must be capable in combination of maintaining by themselves the regular laws. This combined action can never require the assistance of any other process, unless such process can be and is its invariable accompaniment, and then in fact forms part of one group of processes which may conveniently be referred to as a *unit mechanism*. From the fact that each unit mechanism must maintain by itself the regular distribution laws for all temperatures, we can deduce important consequences as to the relative frequencies of occurrence of the constituent processes that compose the unit. In the first instance such a study may even lead to the recognition of a type of process not hitherto suspected to be of importance.

The unit mechanism studied by Klein and Rosseland is based on the well-known inelastic collisions between electrons with more than a certain energy and atoms, whereby an electron in the atom is transferred from one stationary orbit to another of greater energy, apparently without the emission or absorption of any radiation. These are collisions of the first kind. They deduce the existence of "super-elastic" collisions or collisions of the second kind, which form the associated reverse process necessary to complete the mechanism. These consist in the collision of an electron with an excited atom in which the atom returns to normal and the electron goes off with all the superfluous energy in the kinetic form. These ideas have been further developed by Franck* and others, and have already proved of great value in the qualitative interpretation of a variety of phenomena. We shall find it convenient to reformulate the discussion of this mechanism on somewhat broader lines as an introduction to the discussion of another unit mechanism which forms the main theme of this paper.

More recently a second unit mechanism has been studied in detail, of which one constituent is the photoelectric effect. The associated reverse process is the capture of an electron by an ion through the emission of radiation in the encounter.

* Franck, *Zeit. für Phys.* ix. p. 259 (1922); Cario, *ibid.* x. p. 185 (1922); Cario & Franck, *ibid.* xi. p. 161 (1922), xvii. p. 202 (1923).

This has been studied independently by Kramers * and Milne †—the one developing the theory in connexion with the continuous X-ray spectrum emitted by the anticathode of a vacuum tube, and the other with optical absorption coefficients and with Eddington's theory of the interior of giant stars. It should not be overlooked that all these discussions derive from Einstein's classical theory of Planck's Law of Temperature Radiation ‡. The processes of which he treats are the absorption and emission of the optical spectra of atoms, which together form a third unit mechanism.

It is the main purpose of this paper to examine a fourth unit mechanism based on the process of ionization by collision, in particular by electronic impact §. The associated reverse process must clearly be a three-body encounter, which results in the binding of two of the constituents to form a single atom or molecule, the superfluous energy being carried off by the third body. We shall find that the frequencies of these processes can be simply formulated, and that relations hold between the frequencies which are closely analogous to those given by Klein and Rosseland for inelastic and "superelastic" impacts. In order to make practical applications of the theory it is necessary to know from independent evidence the form of the frequency of one of the processes. This is provided to some extent by β-ray phenomena for the frequency of the process of ionization.

It is then possible to examine roughly the relative importance of radiative and radiationless captures and ionizations in controlling the equilibrium of gaseous assemblies at high temperatures, in particular in the reversing layers of stars. We find that for typical reversing layer conditions (pressure of 10^{-4} atmosphere) the radiationless (collision) captures are just negligible. They may, however, be expected to become of importance somewhat greater than the radiative captures at a pressure of about 1 atmosphere.

* Kramers, Phil. Mag. xlvi. p. 836 (1923).

† Milne, Phil. Mag. xlvii. p. 209 (1924).

‡ Einstein, *Phys. Zeit.* xviii. p. 121 (1917).

§ After this paper had been written, a very interesting paper by Becker, *Zeit. für Phys.* xviii. p. 325, published 17 Oct. 1923, came to hand in which the same process is discussed. The author obtains my formula (A) of § 3, but omits to discuss the atomic balance. He thus does not give (B) or observe that probably the correct result is (C), and he does not discuss the relative importance of radiative and radiationless ionizations and captures. The author deals also with radiative captures in the manner of Milne, and with other important points in the theory of statistical equilibrium. [*Note added to proof.* The recent elegant work of Pauli, *Zeit. für Phys.* xviii. p. 272 (1923) on the equilibrium between radiation and *free* electrons belongs to the same order of ideas.]

This result may prove to be of some interest, for it suggests a further quantitative study of the disturbance of the thermodynamic equilibrium of the reversing layer under the influence of a flux of radiation of a temperature greater than its own. It is possible that the next step in the development of Saha's theory lies in this direction, as has already been suggested by H. N. Russell and K. T. Compton.

No attempt is made in this paper to follow up this mechanism into its wider ramifications. They must clearly be of importance in many phenomena. The investigation of the nature of dissociative steady states in the presence of a temperature gradient is as yet an untouched field. It must be tractable at least formally in terms of the frequency coefficients analogous to those whose relations we establish here. But the most interesting field for immediate application would seem to be Rutherford's results on the capture and loss of electrons by α-particles. This will be dealt with in another paper, which will be published shortly.

§ 2. *Klein and Rosseland's Results.*

The frequency of collisions either of the first or second kind (inelastic or superelastic) can be expressed in terms of a certain coefficient, of the dimensions of an area, which is a function solely of the atom and the relative velocity and line of impact of the electron hitting it. This coefficient, which represents the chance of a successful collision, may also depend in an individual collision on the orientation of the axis of the atom relative to the line of impact and on the exact position of the electron in its orbit. The average coefficient, however, which in general is all we shall be concerned with, is obtained by integration over all values of these variables, which are therefore no longer effective. It is of some importance for general applications to secure that all the atomic functions, which are introduced as frequency coefficients, genuinely are atomic functions, and do not depend on extraneous parameters.

Let

$$\mu(\epsilon)d\epsilon = \frac{4\pi y}{(2\pi k\mathrm{T})^{3/2}} e^{-\epsilon/k\mathrm{T}} (2\epsilon)^{1/2} d\epsilon \quad . \quad . \quad (\textit{Maxwell's Law}) \quad (1)$$

be the number of electrons per unit volume whose energies lie between ϵ and $\epsilon + d\epsilon$. These we shall call ϵ-electrons. The total electron density is y, T is the absolute temperature, and k is Boltzmann's constant. If x_1 is the density of any type of atom, which for the moment we suppose fixed in

space or of infinite mass, then the number of collisions per unit volume per second between atoms and ϵ-electrons in which the line of impact lies at a distance between p and $p+dp$ from the atomic nucleus is

$$x_1 \cdot 2\pi p\,dp \cdot \left(\frac{2\epsilon}{m}\right)^{1/2} \mu(\epsilon)d\epsilon. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If $\Sigma_1^2(p,\epsilon)$ is the probability that such a collision is successful in exciting the atom (from state 1 to state 2 say), the number of such successful collisions is

$$x_1 \cdot 2\pi p\,dp \cdot \Sigma_1^2(p,\epsilon)\left(\frac{2\epsilon}{m}\right)^{1/2} \mu(\epsilon)d\epsilon. \quad . \quad . \quad . \quad (3)$$

Writing

$$S_1^2(\epsilon) = 2\pi \int_0^\infty p\Sigma_1^2(p,\epsilon)dp, \quad . \quad . \quad . \quad . \quad (4)$$

we find the total number of successful collisions of the first kind by ϵ-electrons to be

$$x_1 S_1^2(\epsilon)\left(\frac{2\epsilon}{m}\right)^{1/2} \mu(\epsilon)d\epsilon. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This expression is only relevant when $\epsilon \geqslant \epsilon_{12}$, where ϵ_{12} is the extra energy required by the atom in state 2 compared with state 1. When $\epsilon < \epsilon_{12}$, $S_1^2(\epsilon) \equiv 0$. In an exactly similar manner the total number of successful collisions of the second kind by ϵ-electrons can be written

$$x_2 S_2^1(\epsilon)\left(\frac{2\epsilon}{m}\right)^{1/2} \mu(\epsilon)d\epsilon, \quad . \quad . \quad . \quad . \quad (6)$$

in which x_2 is the density of atoms in state 2. These collisions can be effective for any value of ϵ. In the present formulation $S_1^2(\epsilon)$ and $S_2^1(\epsilon)$ have a purely atomic significance; they may be called the mean effective collision areas of the atom for ϵ-electrons. Expressions (5) and (6) differ from those of Klein and Rosseland in the inessential factor $(2\epsilon/m)^{1/2}$, but Klein and Rosseland's coefficients have no very simple meaning.

By considering the conditions for the preservation of Maxwell's Law for the velocity distribution of the electrons, a fundamental relation has been established between $S_1^2(\epsilon)$ and $S_2^1(\epsilon)$. The concentrations x_2 and x_1 are connected according to the ordinary laws of statistical mechanics by the relation

$$x_2/x_1 = (q_2/q_1)e^{-\epsilon_{12}/kT}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

in which q_1 and q_2 are the statistical weights of these states.

The consequent relation between $S_1^2(\epsilon)$ and $S_2^1(\epsilon)$ in the present notation is

$$q_1(\epsilon+\epsilon_{12})S_1^2(\epsilon+\epsilon_{12})=q_2\epsilon S_2^1(\epsilon), \quad . \quad . \quad . \quad (8)$$

which holds for all values of ϵ. Relation (8) guarantees the preservation of the electron distribution laws for all values of T. It also of course guarantees the preservation of (7). For the rate of destruction of atoms in state 1 by this mechanism is

$$x_1\int_{\epsilon_{12}}^{\infty} S_1^2(\epsilon)\left(\frac{2\epsilon}{m}\right)^{1/2}\mu(\epsilon)d\epsilon,$$

and the rate of production

$$x_2\int_0^{\infty} S_2^1(\epsilon)\left(\frac{2\epsilon}{m}\right)^{1/2}\mu(\epsilon)d\epsilon.$$

Using (1) and (7) we see that these rates will balance when

$$q_1\int_0^{\infty}(\epsilon+\epsilon_{12})S_1^2(\epsilon+\epsilon_{12})e^{-\epsilon/k\mathrm{T}}d\epsilon=q_2\int_0^{\infty}\epsilon S_2^1(\epsilon)e^{-\epsilon/k\mathrm{T}}d\epsilon, \quad (9)$$

which is satisfied for all values of T in virtue of (8). It is, however, of interest to observe that (8) can be deduced directly from the fact that (9) must hold for all T. Equation (9) is of the general form

$$\int_0^{\infty} f(\epsilon)e^{-\epsilon/k\mathrm{T}}d\epsilon=0, \ (all\ \mathrm{T}). \quad . \quad . \quad . \quad (10)$$

The necessary deduction is ensured by the following

Lemma.—If $f(\epsilon)$ is a continuous function of ϵ for $\epsilon\geqslant 0$ and

$$\int_0^{\infty} f(\epsilon)e^{-\epsilon/k\mathrm{T}}d\epsilon=0, \ (all\ \mathrm{T}),$$

then

$$f(\epsilon)=0, \ (all\ \epsilon\geqslant 0).$$

This lemma is a direct consequence of Fourier's integral theorem. There is no physical reason to question the applicability of the conditions of the lemma to the function $f(\epsilon)$ derived from the atomic collision areas in (9).

One might naturally hope to be able to deduce in the same way that a relation of the form (8) will hold for the frequencies of every possible switch by collision in an atom with n levels. It appears, however, that no such deduction can be drawn from the general premises of this paper. An atom with n possible levels has $\frac{1}{2}n(n-1)$ possible switches, all of which we must regard as forming one unit mechanism.

In an assembly in equilibrium at a given temperature we have no means of varying the relative frequencies of the constituent processes as we can vary the relative frequencies of processes of different unit mechanisms by changes of concentration. They must be discussed together and analysed, so far as they can be, only by variation of the temperature.

A detailed presentation of the case $n=3$ is instructive. There are three pairs of to and fro switches to consider. Sufficiently slow ϵ-electrons are created only by collisions of the first kind at a rate

$$x_1 S_1^{\,2}(\epsilon+\epsilon_{12})\left\{\frac{2(\epsilon+\epsilon_{12})}{m}\right\}^{1/2}\mu(\epsilon+\epsilon_{12})d\epsilon + x_1 S_1^{\,3}(\epsilon+\epsilon_{13})\left\{\frac{2(\epsilon+\epsilon_{13})}{m}\right\}^{1/2}\mu(\epsilon+\epsilon_{13})d\epsilon + x_2 S_2^{\,3}(\epsilon+\epsilon_{23})\left\{\frac{2(\epsilon+\epsilon_{23})}{m}\right\}^{1/2}\mu(\epsilon+\epsilon_{23})d\epsilon. \quad (11)$$

They are destroyed only by collisions of the second kind at a rate

$$\{x_2 S_2^{\,1}(\epsilon)+x_3 S_3^{\,1}(\epsilon)+x_3 S_3^{\,2}(\epsilon)\}\left(\frac{2\epsilon}{m}\right)^{1/2}\mu(\epsilon)d\epsilon. \quad (12)$$

The condition for the preservation of the regular laws of equilibrium can be written

$$e^{-\epsilon_{12}/kT}F_1^{\,2}(\epsilon)+e^{-\epsilon_{13}/kT}\{F_1^{\,3}(\epsilon)+F_2^{\,3}(\epsilon)\}=0, \ (all\ T), \quad (13)$$

an equation valid only when ϵ is less than the least of ϵ_{12}, ϵ_{13}, and ϵ_{23}. The notation should be sufficiently clear, on remarking that, for example, $F_1^{\,2}(\epsilon)=0$ would be equivalent to (8). When ϵ is unrestricted the first terms in (11) and (12) continue to give the numbers of ϵ-electrons created by the switch $1\rightarrow 2$ and destroyed by $2\rightarrow 1$. There are now in addition

$$x_1 S_1^{\,2}(\epsilon)\left\{\frac{2\epsilon}{m}\right\}^{1/2}\mu(\epsilon)d\epsilon$$

ϵ-electrons *destroyed* by the switch $1\rightarrow 2$, and

$$x_2 S_2^{\,1}(\epsilon-\epsilon_{12})\left\{\frac{2(\epsilon-\epsilon_{12})}{m}\right\}^{1/2}\mu(\epsilon)d\epsilon$$

ϵ-electrons *created* by the switch $2\rightarrow 1$. There are similar terms for the other two switches. If we make the convention that in all cases $F_r^{\,s}(x)=0$, when $x<0$, the new terms above can be accounted for by adding the term $-F_1^{\,2}(\epsilon-\epsilon_{12})$ to (13). The complete form of (13) is therefore

$$-\{F_1^{\,2}(\epsilon-\epsilon_{12})+F_1^{\,3}(\epsilon-\epsilon_{13})\}+e^{-\epsilon_{12}/kT}\{F_1^{\,2}(\epsilon)-F_2^{\,3}(\epsilon-\epsilon_{23})\} + e^{-\epsilon_{13}/kT}\{F_1^{\,3}(\epsilon)+F_2^{\,3}(\epsilon)\}, \ (all\ T, \epsilon). \quad (14)$$

This is equivalent to the three equations

$$\begin{aligned} F_1^2(\epsilon-\epsilon_{12})+F_1^3(\epsilon-\epsilon_{13})&=0,\\ F_1^2(\epsilon)\qquad -F_2^3(\epsilon-\epsilon_{23})&=0,\\ F_1^3(\epsilon)\qquad +F_2^3(\epsilon)\qquad &=0, \end{aligned}$$

of which two only are independent. They reduce to

$$F_1^2(\epsilon)=F_2^3(\epsilon-\epsilon_{23})=-F_1^3(\epsilon-\epsilon_{23}) \quad . \quad . \quad . \quad (15)$$

We can infer that equation (8), $F_1^2(\epsilon)=0$, still holds for $\epsilon<\epsilon_{23}$, but we can infer nothing more as to the vanishing of the F's. The assumption of only two stationary states is equivalent to making ϵ_{23} infinite. It may be noted in passing that if we rule out entirely the possibility of switches by collisions of type $2\rightarrow 3$ and $3\rightarrow 2$, then $F_2^3\equiv 0$, and we can infer that $F_1^2(\epsilon)=0$ and $F_1^3(\epsilon)=0$ for all ϵ. This is the expected inference generalizing (8). But it can only be made when by an artificial limitation we have ruled out the possibility of the cyclic process $1\rightarrow 2$, $2\rightarrow 3$, $3\rightarrow 1$. I cannot find any convincing *a priori* reason to believe that such cycles are not permissible.

It remains to determine the conditions under which the distribution of atoms between the states is preserved. For state 1 this can be written

$$\epsilon^{-\epsilon_{12}/kT}\int_0^\infty F_1^2(\epsilon)\,e^{-\epsilon/kT}d\epsilon+e^{-\epsilon_{13}/kT}\int_0^\infty F_1^3(\epsilon)e^{-\epsilon/kT}d\epsilon=0,$$

and finally reduced to the form

$$\int_0^\infty \{F_1^2(\epsilon)+F_1^3(\epsilon-\epsilon_{23})\}e^{-\epsilon/kT}d\epsilon=0,\ (all\ T). \quad . \quad (16)$$

Condition (16) is equivalent to one of the equations (15) and gives us nothing new. In the same way for states 2 and 3, we get

$$\int_0^\infty \{-F_1^2(\epsilon)+F_2^3(\epsilon-\epsilon_{23})\}e^{-\epsilon/kT}d\epsilon=0,\ (all\ T),$$

$$\int_0^\infty \{F_1^3(\epsilon)+F_2^3(\epsilon)\}e^{-\epsilon/kT}d\epsilon\qquad =0,\ (all\ T),$$

which are also equivalent to components of (15). Equations (15) are therefore the necessary and sufficient conditions for the preservation of the regular equilibrium distribution laws. It may no doubt still be true that the three F's in (15) are severally zero for all ϵ, or in other words that equations of type (8) are true for each type of switch present. But such equations are not a logical consequence of our premises.

In the general case we may expect to obtain only $n-1$ relations between $\frac{1}{2}n(n-1)$ functions F.

Before leaving the consideration of this mechanism, let us remove the restriction that the atoms are fixed. This general case is of practical importance in all except electronic collisions, for it is only then that the random velocities of the atoms are in fact negligible. The relative orbit of the incident electron (or other particle) is determined by the relative velocity V, the usual distance p and the atomic orientation. It is obvious that the average chance of a successful collision of any type must be a function of V and p only. The total number of collisions for which V and p lie between V, $V+dV$ and p, $p+dp$ is given by the well-known formula *

$$4\pi x_1 y \left\{\frac{m\mathrm{M}}{2\pi k\mathrm{T}(\mathrm{M}+m)}\right\}^{3/2} e^{-\frac{1}{2k\mathrm{T}}\frac{\mathrm{M}m\mathrm{V}^2}{\mathrm{M}+m}} \mathrm{V}^3 d\mathrm{V} \cdot 2\pi p\, dp. \quad (17)$$

But the energy of the motion of the system atom-electron relative to its centre of gravity is $\frac{1}{2}\mathrm{M}m\mathrm{V}^2/(\mathrm{M}+m)$ before the encounter has effectively begun, and if the laws of conservation of linear momentum are to be preserved in these processes, it is this energy of the relative motion only, not *e. g.* $\frac{1}{2}m\mathrm{V}^2$, which is available for transformation into atomic energy in a collision of the first kind. Such inelastic collisions will therefore now only begin to occur when

$$\frac{1}{2}\frac{\mathrm{M}m}{\mathrm{M}+m}\mathrm{V}^2 > \epsilon_{12}.$$

Under these conditions (but under no others) the two processes can fit together to preserve the ordinary equilibrium. If ϵ now denotes $\frac{1}{2}\mathrm{M}m\mathrm{V}^2/(\mathrm{M}+m)$, the expression (17) reduces to (2) and the necessary and sufficient condition for preservation of the equilibrium with an atom of two levels is given by (8) as before.

§ 3. *The unit mechanism based on the process of ionization by collision.*

We shall in this section consider only fixed atoms, equivalent to atoms of infinite mass. We know that a process can occur in which an ϵ-electron (or other particle) can knock another electron out of an atom, provided that $\epsilon > \epsilon_0$, where ϵ_0 is the energy necessary to remove this electron. This process of ionization by collision can certainly occur when ϵ only just exceeds ϵ_0, so that there is no reason to suppose that radiation need play any essential part. It seems very probable, from a study of β-ray tracks, that we

* Jeans, 'Dynamical Theory of Gases,' ed. 3. formula (701).

may suppose that the remaining part of the energy $\epsilon-\epsilon_0$ can be distributed in any manner between the two electrons after the collision, and that, whatever ϵ, we may suppose that a process of exchange of this type can occur without the emission or absorption of radiation. Coupled with this process of ionization there must be some process of capture, which for all values of the temperature and concentrations will preserve the laws of dissociative equilibrium. Together these processes of ionization and capture will form a unit mechanism. The process of ionization which we contemplate here is radiationless. So also must therefore be the process of capture. It is not difficult to convince oneself that the only possible (suitable) process of capture is a collision of three bodies, two electrons and one ionized atom, in which the two electrons so interact that one of them is bound by the atom and the other is thrown off with the kinetic energy of both before collision and the ionization energy ϵ_0 thrown in. If the superfluous energy may not be radiated, it can only be carried off by at least one other material body. That such a process, the strict reverse of ionization by collision, occurs can hardly be a novel idea. Its possible great importance does not seem to have been recognized.

The number of collisions with ϵ-electrons and line of impact between p and $p+dp$ is given by (2). Let us suppose here that the only possible result is ionization (provided $\epsilon>\epsilon_0$), after which there will be two free electrons, a new η-electron, and the old one, now an $(\epsilon-\epsilon_0-\eta)$-electron. It is necessary that $\epsilon-\epsilon_0-\eta\geqslant 0$. The probability of such a result must have a definite value depending on p, η, and ϵ. We define $\Sigma_1^2(p,\eta,\epsilon)d\eta$ to be the probability of ionization with the production of a new η-electron with energy between η and $\eta+d\eta$. To find the total production of η-electrons in this way we have to integrate with respect to p. Writing

$$2\pi\int_0^\infty p\Sigma_1^2(p,\eta,\epsilon)dp=S_1^2(\eta,\epsilon), \quad . \quad . \quad . \quad (18)$$

the total is

$$x_1\left(\frac{2\epsilon}{m}\right)^{1/2}\mu(\epsilon)d\epsilon\,.\,S_1^2(\eta,\epsilon)d\eta\,. \quad . \quad . \quad . \quad (19)$$

The total rate of production of ions in this way must be obtained by integrating η from 0 to $\epsilon-\epsilon_0$ and then ϵ from ϵ_0 to ∞. There is a simple physical meaning for

$$\int_0^{\epsilon-\epsilon_0} S_1^2(\eta,\epsilon)d\eta.$$

It is the mean effective collision area for ionization by ϵ-electrons.

The reverse three-body process can be similarly formulated. Consider first of all an ionized atom in process of being hit by a ζ-electron on a line of impact between p_1 and p_1+dp_1. There are

$$x_2 \cdot 2\pi p_1 dp_1 \cdot \left(\frac{2\zeta}{m}\right)^{1/2} \mu(\zeta) d\zeta$$

of these occurrences per unit volume per second. The other electron is to enter into collision on a path on which (if undisturbed) it would reach its apse at a time between τ and $\tau+d\tau$ seconds after the first electron reached its apse. With every collision with a ζ-electron there is therefore associated a volume

$$\left(\frac{2\xi}{m}\right)^{1/2} d\tau \cdot 2\pi p_2 dp_2,$$

in which a ξ-electron may lie whose passage through its apse on a p_2-line of impact would occur in the specified interval. Our expectation of ξ-electrons in this volume is

$$\left(\frac{2\xi}{m}\right)^{1/2} d\tau \cdot 2\pi p_2 dp_2 \cdot \mu(\xi) d\xi.$$

The number of three-body collisions, in which ζ-electrons and ξ-electrons with p_1- and p_2-lines of impact and time difference τ are concerned, is therefore

$$x_2 \left(\frac{2\zeta}{m}\right)^{1/2} \mu(\zeta)\, d\zeta \cdot \left(\frac{2\xi}{m}\right)^{1/2} \mu(\xi)\, d\xi \cdot 2\pi p_1 dp_1 2\pi p_2 dp_2 d\tau. \quad (20)$$

This number has been so specified that it disregards the relative directions of the lines of impact of the electrons and the atomic orientation. Averaged over all such directions and orientations there will be a certain definite probability $\Sigma_1^2(p_1, p_2, \tau, \zeta, \xi)$ that any one of these collisions leads to a successful interaction by which the ζ-electron is bound and the ξ-electron thrown off as a $(\xi+\zeta+\epsilon_0)$-electron. Writing

$$4\pi^2 \int_0^\infty p_1 dp_1 \int_0^\infty p_2 dp_2 \int_{-\infty}^{+\infty} \Sigma_2^1(p_1, p_2, \tau, \zeta, \xi) d\tau = S_2^1(\zeta, \xi), \quad (21)$$

which will then be a purely atomic function of dimensions $[L]^4[T]$, we can express the number of successful triple collisions in which a ζ-electron is bound by the interaction of a ξ-electron in the form

$$x_2 \left(\frac{2\zeta}{m}\right)^{1/2} \mu(\zeta) d\zeta \cdot \left(\frac{2\xi}{m}\right)^{1/2} \mu(\xi)\, d\xi \cdot S_2^1(\zeta, \xi). \quad (22)$$

These collisions each create a neutral atom and a $(\xi+\zeta+\epsilon_0)$-electron at the expense of an ion, a ξ-electron and a ζ-electron.

The appropriate law of dissociative equilibrium * is believed to be

$$\frac{x_2 y}{x_1} = e^{-\epsilon_0/kT}\frac{(2\pi m kT)^{3/2}\sigma}{qh^3} \quad . \quad . \quad . \quad . \quad (23)$$

where h is Planck's constant, σ the so-called symmetry number of the neutral atom, and q the weight of its normal state relative to the ion. If the suggested processes form a unit mechanism they must preserve (23), subject only to certain purely atomic functional relations between S_1^2 and S_2^1. Alternatively (19) and (22) must lead to an equation equivalent to (23) if we prefer to formulate the argument this way round. The necessary functional relations are very simple.

Consider first the preservation of the balance of the electronic distribution laws for η-electrons, $\eta<\epsilon_0$. By the process of ionization new electrons are produced by ϵ-electrons at rate (19) and the old ϵ-electrons are converted to η-electrons when the new ones are $(\epsilon-\epsilon_0-\eta)$-electrons. The combined rate of production of η-electrons in ionization by ϵ-electrons is thus

$$x_1\left(\frac{2\epsilon}{m}\right)^{1/2}\mu(\epsilon)\,d\epsilon\{S_1^2(\eta,\epsilon)+S_1^2(\epsilon-\epsilon_0-\eta,\epsilon)\}d\eta,$$

when $\epsilon<\epsilon_0+\eta$, and is otherwise zero. The total rate of production of η-electrons is therefore

$$x_1 d\eta\int_{\epsilon_0+\eta}^{\infty}\left(\frac{2\epsilon}{m}\right)^{1/2}\{S_1^2(\eta,\epsilon)+S_1^2(\epsilon-\epsilon_0-\eta,\epsilon)\}\mu(\epsilon)\,d\epsilon, \quad (24)$$

per unit volume per second by the ionization process. This holds for all η, but when $\eta<\epsilon_0$ there is no destruction of η-electrons by this process.

Taking now the capture process, we see at once that it produces no η-electrons $(\eta<\epsilon_0)$ for the resulting free electron has always an energy greater than ϵ_0. It destroys each time both a ζ- and a ξ-electron. The total number of η-electrons destroyed by binding (ζ-type) is therefore

$$x_2\left(\frac{2\eta}{m}\right)^{1/2}\mu(\eta)d\eta\int_0^{\infty}\left(\frac{2\xi}{m}\right)^{1/2}S_2^1(\eta,\xi)\mu(\xi)\,d\xi.$$

* See, for instance, Fowler and Milne, Monthly Notices R. A. S., lxxxiii. p. 407 (1923). The only doubtful points in (23) are connected with the values of σ and q. But their precise values are irrelevant here. We are assuming in this discussion that the neutral atom has only one possible stationary state.

The corresponding number destroyed by conversion into fast electrons (ξ-type) is

$$x_2\left(\frac{2\eta}{m}\right)^{1\,2}\mu(\eta)\,d\eta\int_0^\infty\left(\frac{2\xi}{m}\right)^{1/2}S_2{}^1(\zeta,\eta)\,\mu(\zeta)\,d\zeta.$$

The grand total of destructions of η-electrons per unit volume per second is therefore

$$x_2\left(\frac{2\eta}{m}\right)^{1/2}\mu(\eta)\,d\eta\int_0^\infty\left(\frac{2\alpha}{m}\right)^{1/2}\{S_2{}^1(\eta,\alpha)+S_2{}^1(\alpha,\eta)\}\,\mu(\alpha)\,d\alpha, \quad (25)$$

for all values of η. For preservation of the distribution laws we must have

$$x_2\left(\frac{2\eta}{m}\right)^{1/2}\mu(\eta)\,d\eta\int_0^\infty\left(\frac{2\alpha}{m}\right)^{1/2}\{S_2{}^1(\eta,\alpha)+S_2{}^1(\alpha,\eta)\}\,\mu(\alpha)\,d\alpha$$
$$=x_1\,d\eta\int_{\epsilon_0+\eta}^\infty\left(\frac{2\epsilon}{m}\right)^{1/2}\{S_1{}^2(\eta,\epsilon)+S_1{}^2(\epsilon-\epsilon_0-\eta,\epsilon)\}\,\mu(\epsilon)\,d\epsilon,$$
$$(\eta<\epsilon_0). \quad . \quad . \quad . \quad (26)$$

When we use equations (1) and (23), equation (26) reduces to

$$\int_0^\infty e^{-\alpha/kT}(\epsilon_0+\eta+\alpha)\{S_1{}^2(\eta,\epsilon_0+\eta+\alpha)+S_1{}^2(\alpha,\epsilon_0+\eta+\alpha)\}\,d\alpha$$
$$=\frac{8\pi m\sigma}{qh^3}\int_0^\infty e^{-\alpha/kT}\alpha\eta\,\{S_2{}^1(\eta,\alpha)+S_2{}^1(\alpha,\eta)\}\,d\alpha, \ (\eta<\epsilon_0). \quad (27)$$

If equation (27) is to hold for all T, it follows at once by the Lemma that we must have

$$(\epsilon_0+\eta+\alpha)\{S_1{}^2(\eta,\epsilon_0+\eta+\alpha)+S_1{}^2(\alpha,\epsilon_0+\eta+\alpha)\}$$
$$=\frac{8\pi m\sigma}{qh^3}\alpha\eta\{S_2{}^1(\eta,\alpha)+S_2{}^1(\alpha,\eta)\}, \quad . \quad . \quad . \quad . \quad (A)$$

for all α and all $\eta<\epsilon_0$. We may observe that if we do not assume (23), we can deduce its form as a function of T, without of course an explicit value for the constant, from the facts that (26) must be true for all T, and that the atomic coefficients S cannot depend on the temperature and the pressure.

It is necessary in addition that the rates of production and destruction of atomic ions should balance. The condition is easily obtained. It is

$$x_1\int_{\epsilon_0}^\infty\left(\frac{2\epsilon}{m}\right)^{1/2}\mu(\epsilon)\,d\epsilon\int_0^{\epsilon-\epsilon_0}S_1{}^2(\eta,\epsilon)\,d\eta$$
$$=x_2\int_0^\infty\int_0^\infty\left(\frac{2\zeta}{m}\right)^{1/2}\left(\frac{2\xi}{m}\right)^{1/2}\mu(\zeta)\mu(\xi)S_2{}^1(\zeta,\xi)\,d\zeta\,d\xi. \quad (27')$$

Making the same substitutions, this reduces to

$$\int_0^\infty (\epsilon_0+\alpha)e^{-\alpha/kT}d\alpha\int_0^\alpha S_1{}^2(\eta,\epsilon_0+\alpha)d\eta$$

$$=\frac{8\pi m\sigma}{qh^3}\int_0^\infty\int_0^\infty \zeta\xi e^{-(\zeta+\xi)/kT}S_2{}^1(\zeta,\xi)\,d\zeta\,d\xi$$

$$=\frac{8\pi m\sigma}{qh^3}\int_0^\infty e^{-\alpha/kT}d\alpha\int_0^\alpha \eta(\alpha-\eta)S_2{}^1(\eta,\alpha-\eta)d\eta, \quad (28)$$

for all values of T. Therefore by the Lemma

$$(\epsilon_0+\alpha)\int_0^\alpha S_1{}^2(\eta,\epsilon_0+\alpha)\,d\eta$$

$$=\frac{8\pi m\sigma}{qh^3}\int_0^\alpha \eta(\alpha-\eta)S_2{}^1(\eta,\alpha-\eta)\,d\eta, \ (all\ \alpha). \quad (B)$$

It remains to consider the electron balance for $\eta>\epsilon_0$, which in virtue of (B) we shall find to be conserved if (A) holds for all η as well as for all α. Expressions (24) and (25) still give the production by ionization and the destruction by capture. There is now in addition a destruction of η-electrons by ionization at a rate

$$x_1\left(\frac{2\eta}{m}\right)^{1/2}\mu(\eta),\ d\eta\int_0^{\eta-\epsilon_0}S_1{}^2(\alpha,\eta)\,d\alpha, \quad . \ . \quad (29)$$

equal of course to the rate of production of ions by η-electrons. There is also a production by capture. The first argument of $S_2{}^1(\zeta,\xi)$ refers to the electron that is bound. The energy of the electron left free, on binding a ζ-electron in interplay with a ξ-electron, is $\xi+\zeta+\epsilon_0$. If, therefore, $\xi+\zeta+\epsilon_0=\eta$, we have to sum up all triple encounters of the type

$$\zeta,\ \eta-\epsilon_0-\zeta, \quad (0<\zeta<\eta-\epsilon_0),$$

and shall so find that η-electrons are produced at a rate

$$x_2 d\eta\int_0^{\eta-\epsilon_0}\left(\frac{2\zeta}{m}\right)^{1/2}\left\{\frac{2(\eta-\epsilon_0-\zeta)}{m}\right\}^{1/2}\mu(\zeta)\,\mu(\eta-\epsilon_0-\zeta)$$

$$S_2{}^1(\zeta,\eta-\epsilon_0-\zeta)\,d\zeta. \quad (30)$$

The electron equation now contains four terms and equates (24) and (30) to (25) and (29). But on account of (B) the extra terms (29) and (30) balance by themselves. For they will so balance if

$$\frac{8\pi m\sigma}{qh^3}\int_0^{\eta-\epsilon_0}\zeta(\eta-\epsilon_0-\zeta)S_2{}^1(\zeta,\eta-\epsilon_0-\zeta)d\zeta=\eta\int_0^{\eta-\epsilon_0}S_1{}^2(\alpha,\eta)\,d\alpha,$$

which is equivalent to (B). The validity of (A) must therefore be unlimited, and the necessary and sufficient conditions for the preservation of the laws of dissociative equilibrium are that (A) should hold for all α and η, and (B) for all α.

It will be noticed at once that (B) is obtained by equating the first terms only from the two sides of (A), and integrating in a suitable manner. Though it is not a logical consequence of (A) and (B) it seems not at all unlikely that the single relation that really holds is

$$(\epsilon_0+\eta+\alpha)S_1^2(\eta, \epsilon_0+\eta+\alpha)=\frac{8\pi m\sigma}{qh^3}\alpha\eta S_2^1(\eta,\alpha).\ (all\ \alpha, \eta).\quad (C)$$

Equation (C) implies both (A) and (B). It is obviously (C) which would have to hold, if we had to distinguish the two electrons in these processes and no longer regard as interchangeable the bombarding electron (or electron thrown off at high speed) and the electron knocked out of the atom (or bound by the atom). In the case discussed here such a distinction is meaningless, but the arguments apply equally to the case of radiationless dissociations and recombinations in which the three bodies concerned are all different * [for example, perhaps molecular dissociations by electronic or atomic impacts or ionization by bombardments by protons or α-particles]. In such cases the necessary and sufficient relations must be of type (C), and it seems reasonable to suppose that it is equation (C), and not the slightly less restrictive (A) and (B), which holds also in this case.

There is an obvious field for the extension of these arguments to atoms with more than one ionization potential, corresponding to the removal of different electrons, or of the same electron from different orbits. There is also the restriction to fixed atoms to be removed. These are just the extensions which we have made in Klein and Rosseland's work in the beginning of this paper, and they are obviously of some importance. Their consideration cannot be undertaken here.

We note in conclusion that (C) throws perhaps a little light on the meaning of σ and q. The value of σ appears from other chains of reasoning to be equal to the number of electrons in equivalent (most lightly bound) orbits. We should therefore expect S_1^2 to be proportional to σ, as each of these electrons must contribute equally to the mean effective target for the removal of any one of them. The value of q, the weight of the normal orbit of the returning electron, appears to be equal to the number of equivalent

* Provided of course that we may treat the main atoms as fixed.

ways in which the electron can be bound. We should expect S_2^1 to be proportional to q, for each of these ways might be expected to contribute equally to the chances of binding.

§ 4. *The evidence of β-ray results for the form of* $S_1^2(\eta, \epsilon)$ *and* $S_2^1(\eta, \epsilon)$.

It is possible to estimate the mean collision area for ionization with the ejection of an η-electron by a study of the theory and experiments on the passage of β-rays through gases. The classical theory of this phenomenon developed by J. J. Thomson * and Bohr † seems to apply with very considerable accuracy. It leads to the V^4-law for ranges, which is fairly closely obeyed, though the value of the numerical coefficient in the stopping power to which it leads is somewhat too small ‡ (by a factor perhaps of 2 or 3). Moreover, a further slight extension of the theory by the present writer §, in which we require to know only the relative frequencies with which η- and η'-electrons are ejected, leads to the result that the average expenditure of energy by the β-ray per pair of ions made should be four-thirds of the ionization potential. This result seems to be confirmed by the recent experiments of C. T. R. Wilson ‖, in which he finds the value 26 volts per ion-pair in air. Since air is mainly N_2 with a first ionization potential of 17 volts, we should expect from the theory at least 23–24 volts expenditure per ion-pair.

These experimental confirmations refer mainly to high velocities of the electron, but it is with lower velocities, especially those just greater than ϵ, with which we are mainly concerned. More information in this region is greatly to be desired. But even here the β-ray theory gives results which are at least of the expected order. It is shown in the next paragraph that the effective area given for ionization is

$$\frac{\pi\sigma e^4}{\epsilon}\left(\frac{1}{\epsilon_0}-\frac{1}{\epsilon}\right)$$

where e is the electronic charge. This has a maximum when $\epsilon=2\epsilon_0$ whose value is $\pi\sigma e^4/4\epsilon_0^2$. For an atom for which

$$\epsilon_0 = 10 \text{ volts} = 10\times 1{\cdot}591\times 10^{-12} \text{ erg},$$

* J. J. Thomson, Phil. Mag. xxiii. p. 449 (1912).

† Bohr, *ibid.* xxiv. p. 10 (1913); xxx. p. 581 (1915).

‡ C. T. R. Wilson, Proc. Roy. Soc. A. civ. pp. 1, 192 (1923), in particular pp. 196, 199.

§ Fowler, Proc. Camb. Phil. Soc. xxi. p. 521 (1923).

‖ Wilson, *loc. cit.* p. 200.

this area works out at $1{\cdot}56\sigma \times 10^{-16}$ cm.^{2}, so that if allowance is made for a factor of 2 or 3, the theory indicates that the maximum effective area is the whole area of the atom ; this result would seem to be agreeable to the work of Franck and others on ionization potentials. In a first rough survey it therefore seems legitimate to take the classical theory as it stands, for both high and low velocities, as giving correctly the relative frequencies of ejection of η- and η'-electrons, and a numerical coefficient for the absolute frequency at least of the right order.

If then for the moment p denotes the distance of the line of impact of the ϵ-electron from the electron which it is to knock out of the atom, there is a precise relation between this p and η, namely *,

$$p^2 = \frac{e^4}{\epsilon^2}\left(\frac{\epsilon}{\eta+\epsilon_0} - 1\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

or

$$2\pi p dp = \frac{\pi e^4}{\epsilon}\frac{d\eta}{(\eta+\epsilon_0)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

This is the mean effective target of our theory for each equivalent electron. In our notation $\Sigma_1^2(p, \eta, \epsilon)d\eta = 1$ for this region, and is otherwise zero. Thus

$$S_1^2(\eta, \epsilon) = \frac{A\sigma}{\epsilon}\frac{1}{(\eta+\epsilon_0)^2}, \ (A = \pi\epsilon^4), \quad . \quad . \quad . \quad (33)$$

with some doubts as to the numerical factor in A. For the process of capture

$$\frac{8\pi m\sigma}{qh^3}\alpha\eta S_2^1(\eta, \alpha) = (\epsilon_0+\eta+\alpha)S_1^2(\eta, \epsilon_0+\eta+\alpha) = \frac{A\sigma}{(\eta+\epsilon_0)^2}, \quad (34)$$

$$S_2^1(\eta, \alpha) = \frac{qh^3}{8\pi m}\frac{1}{\alpha\eta}\frac{A}{(\eta+\epsilon_0)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

This makes the mean effective collision "time-(area)^2" for capture $\to\infty$ as $\alpha\to 0$ or as $\eta\to 0$. This is perhaps unexpected, but is not in any way physically impossible.

§ 5. *The comparative numerical frequency of radiative (photo-electric) and radiationless (collision) ionizations and captures in a gaseous assembly.*

The calculations that follow do not essentially depend on the foregoing discussion which has established the relation between S_1^2 and S_2^1. To estimate the relative importance of the two processes it is really only necessary to compare

* Fowler, *loc. cit.*

the numbers of ionizations by collision and by the photo-electric effect, and S_2[1] need not be referred to. But it seems proper to give the calculations here, since the preceding considerations seem to give them point. A grasp of the consequences of the idea of the unit mechanism makes it easier to regard the calculation as determining the relative importance of two unit mechanisms as wholes, and it is in this that its main value lies.

Using (1) and (33) we find for the rate of ionization per cubic centimetre per second

$$n_{\text{coll}} = \frac{8\pi\sigma x_1 y}{(2\pi k\mathrm{T})^{3/2}m^{1/2}}\int_{\epsilon_0}^{\infty}\epsilon e^{-\epsilon/k\mathrm{T}}\,d\epsilon\int_0^{\epsilon-\epsilon_0}\frac{\mathrm{A}}{\epsilon}\,\frac{d\eta}{(\eta+\epsilon_0)^2},$$

$$= \frac{8\pi\sigma \mathrm{A}x_1 y e^{-\epsilon_0/k\mathrm{T}}}{(2\pi k\mathrm{T})^{3/2}m^{1/2}}\int_0^{\infty}\left(\frac{1}{\epsilon_0}-\frac{1}{\epsilon_0+\alpha}\right)e^{-\alpha/k\mathrm{T}}\,d\alpha. \quad . \quad . \quad . \quad (36)$$

The integral contains the logarithmic integral and cannot be evaluated in finite terms. When $k\mathrm{T}/\epsilon_0$ is fairly small, it is represented closely by the asymptotic expansion

$$\int_0^{\infty}\left(\frac{1}{\epsilon_0}-\frac{1}{\epsilon_0+\alpha}\right)e^{-\alpha/k\mathrm{T}}\,d\alpha \backsim \left(\frac{k\mathrm{T}}{\epsilon_0}\right)^2 - 2!\left(\frac{k\mathrm{T}}{\epsilon_0}\right)^3 + 3!\left(\frac{k\mathrm{T}}{\epsilon_0}\right)^4 - \ldots,$$

. . . . (37)

with an error always less than the last term retained. The rate of ionization by collision when $k\mathrm{T}/\epsilon_0$ is small enough for the first term of (37) to be a fair representation of the integral is therefore

$$n_{\text{coll}} \backsim \frac{8\pi\sigma \mathrm{A}x_1\, y e^{-\epsilon_0/k\mathrm{T}}(k\mathrm{T})^{1/2}}{(2\pi)^{3/2}m^{1/2}\epsilon_0^2}, \quad \left(\frac{k\mathrm{T}}{\epsilon_0}\ \textit{small}\right), \quad . \quad (38)$$

Now Milne * has shown that the number of photoelectric ionizations per cubic centimetre per second in a gaseous assembly in thermodynamic equilibrium is

$$x_1\int_{\nu_0}^{\infty}\psi(\nu)\mathrm{I}(\nu)\,d\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

where ν_0 is the series limit for the state of the atom concerned, *i. e.* $h\nu_0=\epsilon_0$, and

$$\psi(\nu) = \frac{4\pi^2 m^2\sigma}{cg}\,\mu\left(\frac{c}{h\nu}\right)^3, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

$$\mathrm{I}(\nu) = \frac{2h\nu^3}{c^2}\,\frac{1}{e^{h\nu/k\mathrm{T}}-1}. \quad . \quad . \quad (\textit{Planck's Law}) \quad (41)$$

* *Loc. cit.*

It appears theoretically that μ is a certain function of ν, or better of v the velocity of the corresponding photoelectron. It appears empirically that μ is probably a constant at least in the most important region. The stellar evidence from Eddington's theory of giant stars, together with certain evidence from optical absorption coefficients for resonance radiation, agree in indicating that $\mu = 10^{-4}$ Z, where Z is the atomic number. Taking Z = 1, hydrogen, for illustration, the number of photoelectric ionizations per cubic centimetre per second then reduces to

$$n_{\text{rad}} = \frac{8\pi^2 m^2 \sigma x_1}{qh^3} 10^{-4} kT \int_{\epsilon_0/kT}^{\infty} \frac{dx}{e^x - 1} \quad . \quad . \quad (42)$$

When kT/ϵ_0 is fairly small this is approximately

$$n_{\text{rad}} \backsim \frac{8\pi^2 m^2 \sigma x_1}{qh^3} 10^{-4} kT e^{-\epsilon_0/kT}, \quad \left(\frac{kT}{\epsilon_0} \text{ small}\right) \quad . \quad (43)$$

The ratio $n_{\text{coll}}/n_{\text{rad}}$ is of great interest. We find using (38) and (43)

$$\frac{n_{\text{coll}}}{n_{\text{rad}}} = \frac{10^4 \text{A} q h^3}{2^{3/2}(\pi m)^{5/2}} \cdot \frac{y}{\epsilon_0^2 (kT)^{1/2}} \quad . \quad . \quad . \quad (44)$$

Strictly speaking (44) is valid only for kT/ϵ_0 small, but it will give the correct order for this ratio in a wider range of cases.

If we take the classical value of A, and express all energies in volts we find *

$$\frac{n_{\text{coll}}}{n_{\text{rad}}} = 1{\cdot}15 \times 10^{-16} \frac{qy}{\epsilon_0^2 (kT)^{1/2}}, \quad \text{(energies in volts)}. \quad (45)$$

If we take the case of a typical stellar reversing layer at 10,000°, $kT = 0{\cdot}86$, an electron pressure of 10^{-4} atmosphere, $y = 7{\cdot}86 \times 10^{13}$, and say hydrogen atoms in the Balmer state, $q = 6$, $\epsilon_0 = 3{\cdot}39$ volts, we find

$$\frac{n_{\text{coll}}}{n_{\text{rad}}} = 5{\cdot}1 \times 10^{-3}.$$

Thus in any problem of a stellar reversing layer the effect of the captures and ionizations by collision with electrons is

* I have preferred *at this stage* to compare the relative frequencies of radiative and collision processes on the basis of Milne's semi-empirical formulation of the frequencies of the radiative processes rather than on the basis of Kramer's wholly theoretical discussion, which needs somewhat careful and critical interpretation for application to the cases in point here.

practically nil. The control they will exercise when thermodynamic equilibrium is disturbed by the flow of radiation of a different temperature is negligible *.

The case discussed by Eddington † of the interior of a star turns out to be slightly different. His typical conditions involve an electron density $y = 1{\cdot}356 \times 10^{22}$, and a temperature °C. of $5{\cdot}64 \times 10^6$. The average ionization must have proceeded to a stage such that for the orbits in which we are interested the ionization potentials will lie in the range 600–1000 volts. In such a case we should find

$$\frac{n_{\text{coll}}}{n_{\text{rad}}} = 1{\cdot}2—0{\cdot}42,$$

or 1/6th of these values if we should take $q = 1$. The two types of capture and ionization are now of the same order of frequency, with the radiative type even now somewhat more frequent.

This calculation does not agree with some tentative evaluations of this ratio by Lindemann ‡ in a criticism of Eddington's theory of capture. Lindemann suggests a ratio 10,000 instead of 1, but it is apparent on reading his note that he has ignored the change in target area due to the increase in binding of the relevant electrons, which is allowed for here by the factor ϵ_0^2 in the denominator. This is a factor of the order 10,000 precisely, and its insertion brings his estimate into full agreement with the estimate made here. It should be remembered, however, that whatever the value of the ratio, Eddington's *general* argument that radiative captures will exactly balance photoelectric ionizations is almost certainly sound. Ionizations by collision will balance captures by collision, and Lindemann's criticism so far as it affects the *general* argument appears to rest on a misconception.

The examples above show collision captures to be of somewhat slight importance in the cases specified. This, however, will by no means always be the case. As we descend towards the photosphere from the reversing layer the pressure rises very rapidly indeed compared with the temperature. We should reach a pressure of, for example, 1 or 10 atmospheres with a hardly significant rise in temperature. In these conditions for hydrogen in the Balmer

* It is not difficult to verify in addition that the effect of collisions by the hydrogen or other nuclei will on the same basis be in general negligible compared with that of the electronic collisions.

† Eddington, Monthly Notices R. A. S. lxxxiii. p. 32 (1922).

‡ Lindemann, Monthly Notices R. A. S. lxxxiii. p. 332 (1923).

state we obtain from (45), roughly,

$$\frac{n_{\text{coll}}}{n_{\text{rad}}} = 50—500.$$

These rapid changes in the relative importance of radiative and radiationless processes are probably significant, as we have suggested in the introduction.

§ 6. *Summary.*—Klein and Rosseland's theory of collisions of the first and second kind is discussed and further amplified. It is shown what type of relations can be strictly deduced in the case of atoms with more than two stationary states: also how to formulate the theory when the atoms are no longer assumed to be of infinite mass.

The same ideas are extended to the mechanism of ionization by collision. The reverse process is a three-body collision and the necessary frequency relation is determined.

The theory and experimental results of ionization by β-particles is applied to deduce the form of the frequency function for one of these processes (ionization) and the frequency function for the other is deduced.

The relative importance of collision processes and radiative processes is formulated and discussed in a number of cases, for gaseous assemblies. It is shown that either type may be dominant.

XXIV. *The Capture and Loss of Electrons by α Particles.* *By* Professor Sir E. Rutherford, *F.R.S., Cavendish Professor of Experimental Physics, University of Cambridge* *.

IN a recent paper, G. H. Henderson † has given an account of some very interesting experiments on the capture and loss of electrons by α particles. The photographic effect of a pencil of α rays was examined in a magnetic field by the photographic method, using Schumann plates. In a high vacuum, in addition to the main deflected band due to doubly-charged α particles, there appeared a "midway" band which suffered only half the deflexion of the main band. This band was ascribed to α particles which had captured an electron and which were thus bent by the magnetic field to only half the extent of the main band. As the velocity of the α particles was reduced by increasing thickness of mica over the source, the midway band became

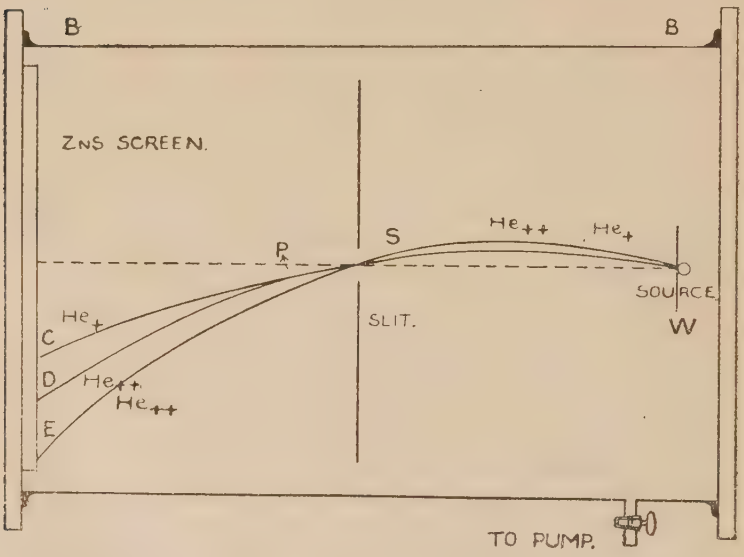
* Communicated by the Author.

† Proc. Roy. Soc. A, cii. p. 496 (1922).

more and more prominent, and ultimately an undeflected band due to neutral helium particles was observed. For the success of these experiments it was essential that the apparatus should be exhausted to the stage of a cathode-ray vacuum. The presence of a small trace of residual gas caused the disappearance of the neutral and midway band. The failure of previous investigators to note the effects observed by Henderson is to be ascribed to the presence of residual gas in the path of the rays in their experiments.

While of course it had always been supposed that the α particle captured electrons near the end of its path, it had not been expected that the α particle could capture an electron in the early part of its range. It was of importance

Fig. 1.



to verify the conclusion of Henderson by the scintillation method where the energy of the particles can be estimated by the brightness of the scintillations and their number determined by direct counting. At the same time it was of much interest to test whether methods could be devised for determining the frequency of capture and loss of electrons by the α particles and its variation with the velocity of the α particle.

The general method * employed is shown in fig. 1. The

* A preliminary account of these experiments was published in the Proc. Camb. Phil. Soc. xxi. p. 504 (1923).

radioactive source consisted of a fine platinum wire W (·3 mm. in diameter), coated with radium B and C, and placed in an exhausted box B. The rays passed through a fine slit S and fell on a zinc-sulphide screen placed inside the box. The scintillations were viewed through a glass plate by a microscope in the usual way. The microscope was arranged to have a vertical motion so that any part of the screen could be brought into view. The slit was equidistant, viz. 8 cm., from the source and screen, and a magnetic field of about 6000 gauss was ordinarily applied perpendicular to the path of the rays. In these experiments it is very important to avoid radioactive contamination of the box and screen. This is very difficult to effect when an uncovered source is used. In the low vacuum required, traces of emanation are usually released from the source, and contaminate the whole box. In addition, if the source is placed in the box soon after removal from the emanation, the recoil of radium B causes a distribution of radioactive matter. Even when the source is not introduced into the box until radium A has practically disappeared, there is still the possibility of contamination due to the β-ray recoil of radium C from radium B. For these reasons, it was essential that the source should be completely covered in. The active wire was placed in a small chamber, covered with the requisite thickness of mica. This chamber could be exhausted during an experiment separately from the main box. The box containing the source and the charcoal tube for exhaustion was fixed rigidly to an ebonite ground-joint, which could be rapidly placed in position in the main box. The latter was initially exhausted by a Gaede pump and then by a Langmuir diffusion pump. The residual pressure of the gas in the box was measured by a Macleod gauge, and two liquid-air traps were in the circuit to prevent mercury vapour from the pump or gauge diffusing into the deflecting box. The field of view of the microscope (1·2 mm. wide) was more than sufficient to take in the whole width of the main band of homogeneous rays.

The distribution of the particles in the deflected beam, found by the scintillation method, is shown in figs. 2, 3, and 4 corresponding to different thicknesses of mica over the source. The emergent range of the α particles was about 3·6 cm. in fig. 2, 1·2 cm. in fig. 3, and 0·46 cm. in fig. 4. The abscissæ represent the actual deflexion of the particles in millimetres in each experiment, but the deflexions are not directly comparable, as the electromagnet was excited by different currents in each case.

In fig. 2 the midway band is deflected to exactly half the extent of the main band, but the number of particles in the

Fig. 2.

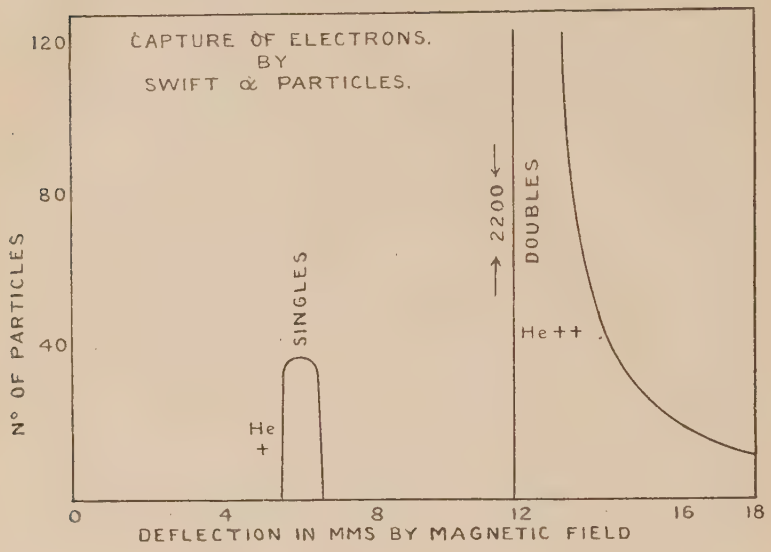
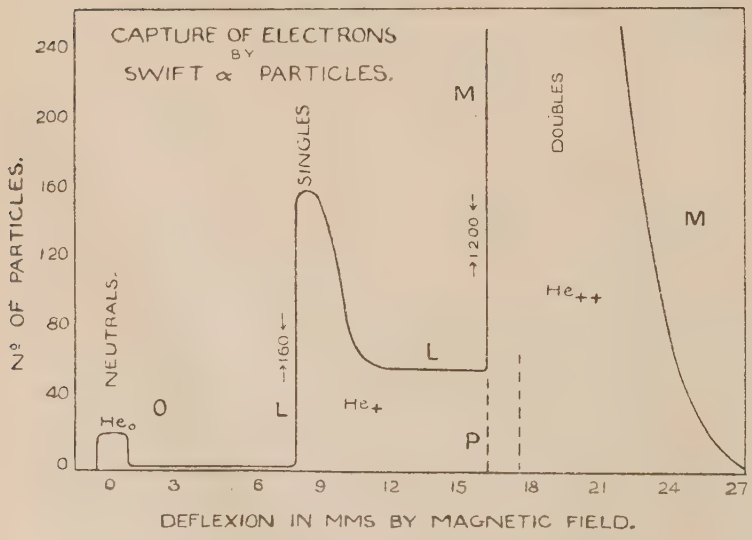


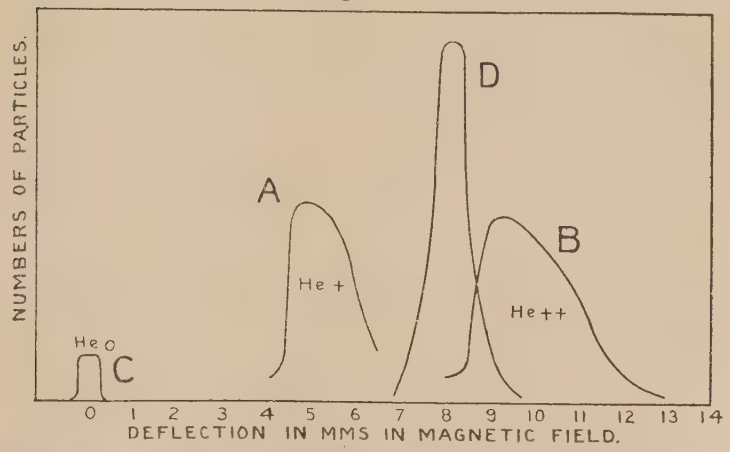
Fig. 3.



band is only 1/67 of that in the main band. With lowering of the range of the emergent α particles, the curves change rapidly in shape. In fig. 3 the width of the deflected main

band MM is much wider than with zero field, showing that the α rays after traversing the mica vary markedly in velocity. The midway band LL begins sharply at the midway point between O and P, but extends with decreasing brightness of scintillations to the main band, where it can no longer be followed. A group of undeflected particles appears at O, while between O and L a small number of weak scintillations was observed. The origin of the latter, which are few in number compared with the neutral band, has been difficult to fix with certainty. They are probably in part due to α particles scattered at the edges of the slits and the sides of the box, and partly due to recoil atoms set in motion by collision with the α particles in their passage through the mica. In fig. 4, for still lower velocities it is

Fig. 4.



seen that the midway band A contains more than half the particles of the main band B, while the undeflected band C becomes relatively more prominent than in fig. 3. There is no longer a sharp inner edge in the two bands, but the maximum number of particles occurs at a considerably lower velocity than the beginning of the bands. The significance of curve D will be discussed later in the paper. It will be clear from these illustrations how rapidly the relative number of particles in the two bands and the distribution of the particles with velocity vary with the emergent range of the particles, *i. e.* with their average velocity.

It will be noted that the width of the band due to the doubly-charged α particles in figs. 3 and 4 is much greater

than the width of the same beam when undeflected by the magnetic field. This shows that the rays issuing from the mica are heterogeneous, consisting of particles with a considerable range of velocity. This heterogeneity of the beam is easily observed, even when the stopping-power of the mica is reduced to 2 cm. I hope in a later communication to discuss this question in more detail when more systematic measurements have been made. In addition to this heterogeneity of the beam due to the passage of the α particles through the mica, the active wire itself is responsible for a similar effect, but on a smaller scale. Some of the α particles from the wire source escape from the back of the wire, and thus are reduced in velocity by their passage through the metal. The relative number of particles escaping in this way which have all velocities from the maximum to zero depends on the diameter of the wire, but under the conditions of the experiment only amounted to a few per cent. of the total number in the pencil. When a magnetic field is applied, these particles give, so to speak, a continuous magnetic spectrum of α rays extending from the edge of the main band in the direction of lower velocities. The heterogeneity in the beam due to the source does not seriously influence the deduction from the experiments discussed in this paper, but is a factor to be taken into account in special experiments where a homogeneous pencil of α rays may be required. This effect could in part be eliminated by the use of specially prepared sources where the activity is concentrated only on the front surface of the source, but such sources are difficult to prepare in sufficient intensity.

Incidentally the determination of the magnetic spectrum of the doubly-charged α particles gave a method of fixing the lowest velocity of the α particle for which a scintillation could be detected. It was found that the scintillations decreased steadily in intensity with increase of the magnetic deflexion. Particles of velocity $\cdot 25V_0$, where V_0 is the maximum velocity of the α particles from radium C, could be readily counted, while particles of velocity $\cdot 15V_0$ gave faint scintillations which could only be counted with difficulty.

The number of particles due to doubly-charged, singly-charged, and neutral helium atoms, as shown in fig. 3, varied in number over such a wide range that sources over a range of intensity of 100 times would be required to determine the number with certainty. To overcome this difficulty, an arrangement equivalent to the rotating wheel

with a slit was employed. Between the outside of the box and the microscope objective a brass plate with a slit of known width described a reciprocating motion between guides. The simple apparatus required was driven by a low-geared motor, so that the slit passed by the objective about four times a second. Using one slit of width 7·5 mm., the reduction ratio for number of scintillations was ·30, with a slit 2·5 mm. about ·10. Usually only the slit of width 7·5 mm. was employed in counting, since the average intensity of the scintillations decreased the narrower the slit. This was due to the fact that it was impossible in the experiment to arrange that the brass plate moved close to the surface of the zinc sulphide. For this reason, some of the light due to a scintillation, which ordinarily entered the objective of wide aperture, was cut off by the plate. This reduction in brightness of the scintillation was so marked that the slits of width 1 mm. or 2·5 mm. could only be used with certainty to count scintillations when α particles of high velocity were used. Since the intensity of the α-ray source decayed to about ·14 of its initial value in the course of two hours, it was generally possible with the aid of the movable slits to compare numbers of α particles in the ratio of 1 to 50 in the course of a complete experiment.

The determination of the curves such as are shown in figs. 3 and 4 involved a large amount of work in counting scintillations. The scintillations became weak in intensity for velocities below $\cdot 2V_0$, and accurate counting trying and difficult.

Electrostatic deflexion of α particles.

While the results obtained by the scintillation method were in general agreement with those obtained by Henderson, using the photographic method, and could be readily interpreted on the view that the α particle captures electrons in its passage through matter, it was of importance to settle definitely whether the particles in the midway beam consisted of singly-charged helium atoms moving with the same velocity as the corresponding particles in the main beam.

For this purpose, the deflexion of the midway band was determined in an electrostatic as well as in a magnetic field. A sheet of mica of about 6 cm. stopping-power was placed over the source, and the distribution of the particles was about the same as that shown in fig. 3. The left edge of the midway band was fairly sharply defined, and corresponded to a velocity of $\cdot 47V_0$. Two parallel brass plates 7 cm. long,

4 mm. apart, were fixed between the source and slit shown in fig. 1, and parallel to the slit so that the deflected beams of rays did not impinge on the side of the plates. By means of an Eversheds motor generator, a P.D. of 3000 volts was applied between the plates. The magnetic field was first adjusted to give a reasonable deflexion of the midway band. The electric field was then added in the highly exhausted box, and the shift of the edge of the midway band was noted on reversal of the electric field. Similar observations were made on the edge of the main band. The settings of the cross wire of the microscope on the edge of the bands could be made with precision. The change of deflexion of the main band by reversal of the field due to 3000 volts was 3·27 mm., and for the midway band 1·63 mm. or almost exactly half. The deflexion of the highest velocity particles in the midway band in a magnetic field, as we have seen, is exactly half of the corresponding particles in the main beam.

Suppose M, V, E be the mass-velocity and charge of the α particles in the main beam, and m, u, e the corresponding values for the particles in the midway beam.
From the observed magnetic deflexions,

$$MV/E = 2mu/e.$$

From the observed electrostatic deflexions,

$$MV^2/E = 2mu^2/e.$$

It thus follows that $u = V$

and $e/m = \frac{1}{2}E/M.$

It is thus clear that the particles of the midway band have the same velocity as the corresponding particles in the main beam—a fact confirmed by the equal brightness of the scintillations,—but the value e/m is half of that for the ordinary α particle. It seems quite certain from these results that the particles in the midway band are singly-charged atoms of helium, *i. e.* helium nuclei which have captured one electron. It is thus natural to suppose that the undeflected particles are neutral helium atoms arising from the capture of two electrons by the α particles.

Mean free path for capture and loss.

It is to be supposed that the α particle occasionally captures an electron, and this electron may be subsequently lost by collision with the molecules. We shall see later that, for high-velocity particles, the average distance traversed by

the α particles in the material before capturing an electron or losing its captured electron is small compared with the range of the α particle in the material. We may suppose that for a definite velocity the He_{++} particle has a mean free path λ_1 cm. in the material before capturing an electron. No doubt some of the particles have much shorter and others much longer paths than the average before capture, the relative numbers being determined by the law of probability. Similarly, it may be supposed that the He_{+} particle has a mean free path λ_2 cm. before losing its attendant electron by collision with the molecules.

It will be seen later that the interchanges of charge of the α particle occur more than a thousand times in its range. It is thus clear that a temporary equilibrium must exist between the numbers of N_1 of He_{++} particles and the number N_2 of He_{+} particles for any given velocity, such that the number of captures is nearly equal to the number of losses in traversing a small thickness dx of the material. Consequently

$$N_1 dx/\lambda_1 = N_2 dx/\lambda_2,$$

or

$$N_2/N_1 = \lambda_2/\lambda_1.$$

It is clear that the ratio N_2/N_1 can be directly determined for any velocity by comparing the number of singly- and doubly-charged particles escaping from the mica in a vacuum over the same small range of velocities. The ratio λ_2/λ_1 is thus known.

This relation obviously applies not only to a definite beam of homogeneous rays, but to each constituent of a pencil of heterogeneous rays such as are shown in figs. 3 or 4. If the distribution curves are obtained accurately for He_{++} and He_{+}, it is clear that the ratios λ_2/λ_1 can be obtained over a considerable range of velocity from a single experiment.

The mean free path λ_2 for loss of an electron from He_{+} can be directly measured in the following way. Suppose the microscope is placed in such a position as to include the particles on the inside edge L of the midway band (fig. 3) and the number of scintillations counted in a high vacuum. When a gas at low pressure is introduced into the box, some of the He_{+} particles lose an electron by a collision, and are deflected away from the field of view of the microscope. For example, the loss of an electron at P (fig. 1) will cause the particle to strike the screen at D instead of at C. It was found that the number of scintillations decreased nearly according to an exponential law with the pressure of the gas,

and ultimately became too small to count for a pressure of gas not sufficient to alter sensibly the velocity of the rays in traversing the gas. In these experiments, appropriate quantities of the dry, purified gases under examination were successively introduced by means of side tubes. It was found essential to have a liquid-air trap between the box and the Macleod gauge in order to prevent any mercury vapour entering the box. If the Langmuir pump were cut off from the highly exhausted box and the liquid air then removed from the trap between the box and the Macleod gauge, there was a rapid decrease in the intensity of the midway band as the pressure of mercury vapour in the box gradually rose. This experiment shows how effective is even a small pressure of mercury vapour in converting He_+ into He_{++}. For the higher velocities of the α particle the conversion of He_{++} into He_+ in the passage of the rays through the gas did not appreciably affect the result. With diminished velocity, this effect became noticeable. For example, using α particles of maximum velocity $\cdot 47V_0$ corresponding to fig. 3, the number did not fall to zero with increasing pressure of the gas. These residual particles were no doubt in part due to the continuation of the distribution between O and L, shown in fig. 3, and probably also to the conversion of He_{++} into He_+ in their passage through the gas, for in the case under consideration the mean free path for capture was only 7·5 times that for loss for the swiftest particles. An estimate of this effect was made by moving the microscope towards O by the width of its field of view and counting the scintillations at that point. When this correction was made, the number fell off according to an exponential law within the limit of experimental error.

The number of particles N_p remaining at a pressure p mm. at 0° C. is given by $N_p/N_0 = e^{-\mu pl}$, where μ is a constant and l cm. the effective length of gas traversed. This length was somewhat less than the actual distance between the source and screen, for a correction was necessary owing to the finite width of the field of view of the microscope. It is obvious that a particle might not be deflected from the field of view if it captured an electron when near the zinc-sulphide screen. The magnitude of this correction depended on the strength of the magnetic field as well as on the width of the field of view, and was easily allowed for. It is clear that the mean free path for loss is given by $1/76\mu$ in terms of millimetres of the gas at N.P.T. For example, for a velocity $\cdot 47V_0$ the number of particles were reduced to half their initial value

for a pressure of air of 1/50 mm. The effective value of l was 13·0 cm. Consequently the mean free path for captures in air was 5/1000 mm. at N.P.T.

The removal of the electron from the He_+ particle corresponds to a process of ionization of the moving particle itself. It is to be anticipated that this ionization should obey laws similar to those found for the ionization of a gas by the swift α particle. This is found to be the case, for the value of λ_2 was approximately proportional to the velocity of the particle between the velocities $\cdot 94V_0$ and $\cdot 47V_0$. This is in accord with the well-known fact that the ionization produced in a gas by an α particle is inversely proportional to its velocity over this range. This analogy was still further emphasized by comparing the mean free path for loss of an electron in hydrogen and helium as well as in air. It is known that the ionization in hydrogen and helium per unit path is about one-quarter of its value in air for the same velocity. The mean free path in hydrogen was found to be 4 to 5 times longer than in air. The few experiments made with helium indicated that its mean free path was longer than in hydrogen and 5 to 6 times its length in air.

It will be seen that the mean free path for loss is measured in air or other gas, while the ratio λ_2/λ_1 is measured in mica or other solid material. It was, however, found experimentally that the ratio λ_2/λ_1 observed with mica alone, for a velocity of rays of $\cdot 47V_0$ changed only slightly when a thin layer of celluloid, aluminium, or silver was placed over the mica plate. The thickness of the layer—of the order of 1 mm. stopping-power for α rays—was sufficient for a new equilibrium to be set up between He_{++} and He_+ particles, but not enough to alter markedly the velocity of the issuing rays. Since little change * was observed for such a wide range of average atomic weight of absorber, we may conclude that the radio λ_2/λ_1, if it could be measured entirely in air, would be nearly the same as that observed for mica in which oxygen is an important absorbing constituent. The validity of this relation for all velocities requires further experimental confirmation, but it is probably not seriously in error. The approximate constancy of the ratio λ_2/λ_1 for different elements is a matter of considerable interest, but requires further

* When a thin sheet of gold was placed over the mica, the number of He_+ particles was approximately doubled, indicating that the ratio λ_2/λ_1 does vary appreciably in this case. A more detailed investigation of the variation of this ratio with the atomic weight of the element is being undertaken by Mr. Henderson in the University of Saskatchewan.

verification by a more accurate method than that of counting scintillations.

The values of $\lambda_2/\lambda_1 = N_2/N_1$ for mica were directly measured for three velocities, viz. ·94, ·76, ·47V_0 in a high vacuum, while the mean free path in air for conversion of He_+ into He_{++} was obtained for the same velocities. The results are given in the following table, where the mean free path both for capture and loss is given in terms of mm. of air at N.P.T. :—

TABLE I.

Velocity in terms of V_0.	λ_2/λ_1 for mica.	Mean free path for loss in air.	Mean free path for capture in air.
·94	1/200	·011 mm.	2·2 mm.
·76	1/67	·0078 „	0·52 „
·47	1/7·5	·0050 „	·037 „

The velocity V_0 of the α particles from radium C is $1{\cdot}922 \times 10^9$ cm.

Over the ranges examined, viz. from ·94V_0 to ·47V_0, the ratio λ_2/λ_1 varies very rapidly with the velocity. If we suppose the variation is expressed by V^n, the average value of n from the data obtained is about 4·6, or the ratio λ_2/λ_1 varies roughly inversely as the fifth power of the velocity. Since λ_2 varies nearly as the first power of V, it is seen that λ_1, the mean free path for capture, varies as $V^{5\cdot6}$, or roughly as the sixth power of the velocity. These relations are only approximate ; accurate values will require a large amount of careful counting of scintillations over a wide range of velocity of the α particles.

A number of experiments were also made with thorium C as a source instead of radium C. For this purpose a nickel wire of ·3 mm. diameter was exposed in a solution of radiothorium. It is well known that the radiation from this source consists of 65 per cent. of α particles of range 8·6 cm. and 34 per cent. of particles of range 4·8 cm. A thickness of mica of 1·1 cm. stopping-power was placed over the source, so the emergent α rays were of range 7·5 and 3·7 cm. respectively. It was possible in a strong magnetic field to resolve completely the midway and main bands due to the two sets of α rays, so that the particles could be independently counted. Unfortunately, with the

active matter available, it was impossible to concentrate sufficient activity on the fine nickel wire to obtain a sufficient number of scintillations per minute for accurate counting in the midway band with the faster particles. The average number was only 6 to 8 per minute in the various experiments. The ratio $\lambda_2/\lambda_1 = 1/330$ was found for the 7·5 cm. particles, *i. e.* for a velocity $1{\cdot}02V_0$. The ratio calculated from the results with radium C by means of the power law was about 1/290. The agreement is as good as could be expected, considering the small number of scintillations which were counted.

It was of interest to note that, although the number of particles in the main band of range 3·7 cm. was only about one-half of those of range 7·5 cm., the number of particles in the corresponding midway bands was nearly in the ratio of two to one. Such a result is to be anticipated from the data previously discussed. There is no evidence that the α particles from thorium C show any difference with regard to frequency of capture and loss from the α particles of radium C of corresponding velocites.

Capture and loss at low velocities.

A large number of experiments have been made to determine the distribution curves of the particles for low velocities in order to estimate the ratio of He_+ to He_{++} over a wide range of velocities from a single curve. One of these distribution curves is shown in fig. 4 corresponding to α particles of emergent range about 4·6 mm. It is seen that the particles composing the midway band A and the main band B are very heterogeneous. The high-velocity edges of these two bands are not so sharply defined as for higher velocities, so that it is difficult to determine directly the mean free path for loss by introducing gas into the apparatus. In addition, since the mean free path for capture and loss is of the same order of magnitude, complications arise from the conversion of He_{++} to He_+ and of He_+ to He_0 in the passage of the rays through the gas.

The following procedure was adopted to compare the relative number of He_+ and He_{++} for different small velocities. A sufficient magnetic field was applied to give a convenient deflexion, generally about 10 mm., of the edge of the midway band. The microscope was fixed at a certain position and the scintillations counted. The current through the magnet was then adjusted to give exactly half the magnetic field. This brought the He_{++} particles over the

same small range of velocity in the field of view of the microscope, and their number was counted. In this way the ratio of singly- to doubly-charged particles was determined over the whole range of velocities available. The advantages of this method of comparison were many. The ratio required of the number in the two bands was directly obtained by counting successively and under identical conditions on the same part of the screen. These conditions are particularly advantageous with weak scintillations where counting is difficult, and the actual number counted is somewhat dependent on the luminosity of the screen and fatigue of the eyes.

The maximum velocity of the particles in the bands was $\cdot 37 V_0$. The maximum of the midway band occurred at a velocity $\cdot 32 V_0$ and for the main band $\cdot 35 V_0$. The singly- and doubly-charged particles were equal in number at a velocity $\cdot 29 V_0$. Assuming that λ_1/λ_2 varies as $V^{4\cdot 6}$, the calculated velocity for equality in number is $\cdot 30 V_0$— a value in good accord with that observed.

It was possible to count with some certainty down to a velocity $\cdot 22 V_0$. Below this velocity the particles were faint and few in number, and difficult to count with accuracy. The results obtained are illustrated in the following table :—

Table II.

Velocity.	Observed $N_2/N_1 = \lambda_2/\lambda_1$.	λ_2/λ_1 Calculated values.
$\cdot 47 V_0$	·133	·133
$\cdot 32 V_0$	·53	·68
$\cdot 29 V_0$	1·00	1·2
$\cdot 27 V$	1·5	1·7
$\cdot 23 V_0$	3·0	3·6

The values for $\cdot 47 V_0$ are taken from Table I. for comparison. The calculated values in the third column are deduced from the value for $\cdot 47 V_0$, assuming that $\lambda_1/\lambda_2 \propto v^{4\cdot 6}$. Considering the wide range of extrapolation and the difficulties of the experiment, the agreement is as good as can be expected, indicating that the velocity law holds approximately over the wide range from $\cdot 23 V_0$ to V_0. Comparing the values of λ_2/λ_1, viz. 1/200 for $\cdot 94 V_0$, and the value 3·0 for $\cdot 23 V_0$, the

index of the power law is 4·54. It is thus seen that the ratio of singly- to doubly-charged particles has been examined over a range of more than 600 times. If we assume that the mean free path for loss varies directly as the velocity down to the velocity $\cdot 23V_0$, the mean free path for capture varies in the experiments over a range of about 2500 times.

Undeflected particles.

Undeflected helium atoms were first noted in considerable numbers in the experiment corresponding to fig. 3, where the maximum velocity of the α particles was $\cdot 47V_0$. The scintillations were for the most part faint, and were about 1/140 of the number of α particles in the main band. In the experiment, illustrated by fig. 4, for still lower velocities the number of undeflected particles was relatively greater, corresponding to about 1/40 of the total number of α particles.

No doubt the undeflected particles mainly arise from the low-velocity particles which carry a single charge. From the average brightness of the scintillations, I should judge the mean velocity of the particles lay between $\cdot 25V_0$ and $\cdot 30V_0$, but a number of very faint particles corresponding to very low velocities were noted under exceptionally good conditions for counting. No doubt the neutral particles are very heterogeneous in velocity, but, from the nature of the experiments, it is difficult to estimate their distribution with velocity.

By introducing a small quantity of gas into the apparatus, the number of particles in the neutral band diminished and practically disappeared for a pressure of air of about 3/100 mm. The actual stopping-power of this pressure of residual gas is only about 1/160 mm. of air at N.P.T., and thus is much too small to reduce seriously the velocity of the particles.

It seems clear that the disappearance of the neutral band is due to the conversion of neutral into singly-charged helium atoms. Some experiments were made to estimate the mean free path in air of the conversion He_0 to He_+. The observations are difficult on account of the weakness of the scintillations, but it was estimated that the mean free path for conversion of He_0 into He_+ was about 1/100 mm. or about 1/5 of the mean free path for conversion of He_+ into He_{++} for a velocity $\cdot 47V_0$. No certain difference was noted in this respect between the neutral particles produced under the conditions illustrated in figs. 3 and 4.

Singly-charged particles from naked sources.

It was of great interest to examine whether the bare platinum source, without any mica covering, gave any singly-charged helium atom. The observations were made rapidly after the wire was introduced into the apparatus, for under such conditions the general contamination due to the bare source is not serious. It was found that the number of singly-charged particles was about the same in number as if the wire had been covered with a thickness of mica of 3 or 4 mm. stopping-power to give the equilibrium distribution. This was a surprising result when it is considered that the mean free path for capture for such high-velocity particles is about 3 mm. of air and the amount of active matter is too small to form even a film of one molecule thick over the surface of the wire. These He_+ particles could not be due to the heterogeneity of the rays produced by the source, which has already been referred to, for only the swiftest α particles were counted by the microscope. When the wire is exposed to the emanation, the radium A atoms are deposited on the surface, and some of the radium B atoms are thus driven into the wire by recoil. Consequently, some of the α particles escaping from radium C have to pass through a small thickness of platinum. Calculation shows that this thickness is much too small to set up an equilibrium between He_+ and He_{++}. However, in order to test the matter further, a source of radium C was obtained by electrolysis on nickel. In this case the radium C is deposited directly on the surface of the nickel, and the effect due to recoil should be absent. Again, the number of He_+ was about the equilibrium value.

It is very difficult to believe that these He_+ particles come directly from the nucleus; and, even if this be assumed, it is a curious coincidence that the number should be about that required for equilibrium between He_+ and He_{++} in their passage through mica. We are driven to the conclusion that at any rate a partial equilibrium is set up by the passage of the α particle through the dense distribution of the electrons round the nuclei from which they are expelled. It is well known that the collisions due to an α or β particle in escaping from the nucleus of an atom appear to be much more effective than if the particle passes into the atoms from the outside. It may well be that some of the particles may gain or lose an electron several times before they escape from the parent atom, and thus an approximate equilibrium may be set up between the singly- and doubly-charged

particles. For example, it is to be expected that this interchange of electrons would most readily occur in the groups of electrons whose orbital velocity is about the same as the velocity of the α particle.

The effect of gas in the path of the α particles.

Consider an experiment similar to that illustrated in fig. 4, where A, B, and C represent the distribution of He_+, He_{++}, and He_0 in a vacuum. On adding gas, these three bands disappear and are replaced by a single comparatively narrow band shown in D. To obtain this band, the pressure of air in the chamber was 1·1 mm., corresponding to a stopping-power of ·23 mm. of air for the α particle. Since the mean free path for capture for the highest velocity of particles present, viz. $\cdot 37V_0$, is probably about ·008 mm., it is seen that the average number of captures and losses in the air for an α particle of this velocity is about 30, and still more for the slower particles. When the captures of an α particle in traversing the gas are as numerous as this, each α particle of definite velocity in a magnetic field is deflected as if it carried a charge between e and $2e$, the actual magnitude depending on the ratio of the mean free paths for capture and loss.

It can be readily calculated from the observed distributions with velocity of He_+ and He_{++} in a vacuum, that the particles after traversing the gas should be mainly concentrated in a comparatively narrow band such as is shown in curve D.

Consider α particles of velocity V whose mean free paths in the gas are λ_1 and λ_2 for capture and loss respectively. Since there are many interchanges of charge in traversing the gas, the magnetic deflexion will correspond to particles of velocity V of which the average charge is

$$\frac{\lambda_1 2e + \lambda_2 e}{\lambda_1 + \lambda_2} \quad \text{or} \quad e\left(1 + \frac{\lambda_1}{\lambda_1 + \lambda_2}\right).$$

The magnetic deflexion will thus be proportional to

$$\frac{e}{V}\left(1 + \frac{\lambda_1}{\lambda_1 + \lambda_2}\right).$$

From the experimental data for λ_2/λ_1 given in Table II., and adding the value for the velocity $\cdot 37V_0$, it can be calculated that the magnetic deflexion of α particles of velocities ·37, ·32, ·29, ·27, $\cdot 23V_0$ is proportional to 483, 516, 517, 518, 543 respectively in arbitrary units. Now, the velocity of the α particles in the main beam B lies mainly between the

velocities ·23 and ·37V_0. It is thus seen that the deflected band with gas in the vessel should be confined within a much narrower range of velocity than the main or midway band in a vacuum. This, as we have seen, is found to be the case experimentally. From the calculations, it seems clear that the concentration of particles should be very marked for a very narrow pencil of α rays. Whatever the concentration, the band cannot be narrower than the normal width of the beam in a vacuum with no magnetic field. It is intended later to examine the concentration with very narrow beams, as it may be expected not only to afford a definite test for the reliability of the data for capture and loss at low velocities, but also to throw light on the question whether one α particle differs from another with regard to frequency of capture or loss. This possibility has been suggested by P. Kapitza * as an explanation of the different curvatures observed in α-ray tracks when acted on by intense magnetic field.

This concentration effect, which is so intimately connected with the frequency of capture and loss at low velocities, gives a very simple but direct method of testing the important question whether an α particle captures electrons in hydrogen as well as in air. Since the mean free path for loss in hydrogen is about five tines as long as in air, hydrogen was introduced into the vessel at a pressure of about 5 mm., equivalent to the pressure of 1 mm. used for air. Under such conditions the curve for hydrogen was very similar to that obtained for air, and showed a similar concentration. This affords a definite proof that the α particle captures electrons in hydrogen and that the ratio of the mean free path for capture to that for loss is of the same order as for air. This result will be seen to be of some importance in the discussion of the mechanism of capture.

Number of interchanges.

From the data given in this paper, it is clear that the interchange of charges presented by $He_{++} \rightleftarrows He_{+}$ is predominant down to a velocity ·29V_0 where the number of H_+ and H_{++} are equal. Below this velocity the interchange $He_{+} \rightleftarrows He$ begins to be important, and no doubt becomes predominant for low velocities of the α particle. It is clear also that the interchanges of charge of the α particle are very numerous in its flight. A rough estimate of the number of

* P. Kapitza, Camb. Phil. Soc. xxi. p. 511 (1923).

captures between any specified velocities of an α particle can be made in the following way. It is convenient to express the velocity of the α particle and its mean free path for capture and loss as multiples of the corresponding values for the maximum velocity V_0 of the α particle from a bare di um C source.

If $x = V/V_0$, the mean free path λ_1 for capture is given by $\lambda_1/L_1 = x^{5\cdot6}$ where L_1 is the mean free path for capture for a velocity V_0. From the cube law connecting the velocity of an α particle with its range, $R = R_0 x^3$ where R is the range of α particles of velocity V, and R_0 the maximum range for velocity V_0. Differentiating, $dR = 3R_0 x^2 dx$, the number of captures in the distance dR,

$$= \frac{dR}{L_1} = \frac{3R_0}{L_1} x^{-3\cdot6} dx.$$

The total number of captures between velocities x_1 and x_2

$$= \frac{3R_0}{2\cdot6 L_1}(x_2^{-2\cdot6} - x_1^{-2\cdot6}).$$

Take $L_1 = 3\cdot1$ mm., $R_0 = 7\cdot06$ cm., the number of captures between velocities V_0 and $\cdot29V_0$ is seen to be 630. This is an over-estimate, for we must remember that every capture is followed by a loss. By taking account of the variation of mean free path for loss over the path, I estimate that on the average 590 captures occur from the beginning of the range of the α particle to the velocity $x = \cdot29$ where the mean free paths for capture and loss are equal. It can also be shown that on the average for the range traversed, viz. 6·89 cm., the α particle remains doubly charged for a total distance of 6·39 cm. and singly charged for a distance ·50 cm. Too much stress must not be laid on this calculation, for it assumes the accuracy of Geiger's rule connecting range and velocity, viz. $V^3 \propto R$. Blackett * has recently shown that this law breaks down in the last centimetre of the range, and the experimental results are more nearly expressed by a relation of the form $V^{-1\cdot5} \propto R$. It follows that the range of particles falls off more slowly with velocity in the last centimetre than is calculated on Geiger's rule, and consequently the number of captures have been underestimated. Since the α particle at velocity $\cdot29V_0$ makes 300 captures and losses per mm. of path, it is easily seen that the change in the law of absorption will cause a considerable increase in the total number of captures. In addition, the mean free path for

* Blackett, Proc. Roy. Soc. A, cii. p. 294 (1922); ciii. p. 62 (1923).

conversion $He_0 \rightarrow He_+$ has been shown to be small (see p. 291). We shall not be much in error if we suppose that the interchange of charges must occur several thousand times in all during the flight of the α particle. It is probable that the number of captures, for complete absorption of the α particle, is of the same order for all the elements including hydrogen, though no doubt the total number will vary somewhat for the different elements probably in the same sort of way that the total ionization of the α particles is known to vary.

When we consider the frequency of capture or loss of electrons by the α particle, we should not expect to notice any appreciable change in the power of penetration of particles in the main, midway, or neutral bands, provided we compare particles of identical velocity. Henderson (*loc. cit.*) made some comparisons of this kind, but with indefinite results. If any marked difference in penetration were to be observed, it would afford strong evidence of some individual differences in the α particles, such as has been suggested by Kapitza, with regard to capture or loss or both.

Comparison with Positive Rays.

Observations on the capture and loss of electrons by the α particle have been studied in this paper between velocities V_0 and $\cdot 23V_0$, *i.e.* between $1\cdot 922 \times 10^9$ and $4\cdot 4 \times 10^8$ cm. per second. The phenomena of capture and loss shown by the α particle are very similar to those shown by the positive rays in a discharge-tube. The theory of this has been worked out by W. Wien, and an interesting account of the various investigations made to determine the mean free path of charged hydrogen atoms and neutral hydrogen atoms in various gases have been given in a recent paper by E. R. Rüchardt *. The maximum velocity of the hydrogen atoms used in his experiments was about $2\cdot 26 \times 10^8$ cm. per second corresponding to a P.D. of 35,000 volts. The experiments on the α particle have thus been made at much higher velocities than for hydrogen atoms, and the highest velocity examined by Rüchardt is only one-half of the lowest velocity of the α particle studied in the present paper. In order to obtain velocities of H_+ equal to the α particles from radium C, an accelerating potential of 2·5 million volts would be necessary. From the results of Rüchardt on hydrogen rays it can be deduced that the mean free path for capture and loss in nitrogen is about the same, viz. about 1/2000 mm. at N.P.T.

* *Ann. de Phys.* lxxi. p. 322 (1923).

for a velocity of $2{\cdot}26 \times 10^8$ cm. per second. This corresponds to a velocity $\cdot 12V_0$ in terms of the α particle.

Now, it is to be expected that the interchange $He_+ \rightleftarrows He_0$, if governed mainly by velocity, must behave very similarly to the interchange $H_+ \rightleftarrows H_0$, with the difference that the ionizing potential of helium is higher, about 24·5 volts, than the ionizing potential of hydrogen, 13·5 volts. We should thus expect from the experiments on hydrogen rays that the mean free path of He_+ and He_0 should be equal for a velocity somewhat higher than in the case of hydrogen rays. I estimate its probable value to be $\cdot 16V_0$.

In the case of the α particles, the actual velocity for equality has not so far been measured, but the rough results obtained of the relative numbers of He_0 and He_+ are not inconsistent with such a value. It is of interest to note that the mean free path for the conversion of He_0 into He_+ was estimated to be about 1/1000 mm.

It is not to be expected that the variation with velocity of the mean free paths for capture and loss, observed for hydrogen rays, should follow the relations observed for swift α rays. From the data given by Rüchardt for hydrogen rays, no very definite conclusions can be drawn on the variation with velocity of the mean free paths in various gases. In the table, however, given in his paper (p. 409), referring to the passage of hydrogen rays through oxygen, it can be deduced that the ratio of the mean free paths for capture and loss varies roughly as $V^{4\cdot6}$ for a range of velocities corresponding to 24,500 and 36,800 volts. This law is the same as we have observed for high-velocity α particles, but the agreement may be only accidental, since the corresponding data for nitrogen at lower velocities does not accord with such a relation.

Discussion of results.

When an α particle captures an electron, it presumably falls in the majority of cases into the same orbit round the helium nucleus which characterizes an ionized helium atom. The ionization potential under these conditions is believed to be 54 volts. When the α particle with the attendant electron passes through the atoms of a gas in its path, it will not only ionize the gas, but will occasionally be itself ionized, *i. e.* will lose its attendant electron. We shall see that the mean free path for loss calculated on these assumptions is of about the magnitude observed experimentally. In making

the calculation, it is necessary to draw a sharp distinction between the primary and secondary ionization * produced by an α particle. This point has been discussed recently by R. H. Fowler †. Consider for simplicity the ionization in hydrogen. Corresponding to the maximum velocity V_0 of radium C, the α particle produces 528 ions per mm. of path, and of these only 1/4·4, *i. e.* 120, are primary. Now, the mean free path in hydrogen for loss of an electron from He_+ is for this velocity about ·060 mm. In this distance, where one He_+ atom is ionized the α particle produces 7·2 primary ions. Taking the ionization potential of hydrogen as 16 volts and for He_+ as 54 volts, the numerical relation observed is in fair accord with calculation. In order to calculate the chance of ionization of the He_+ atom, it is simplest to suppose that the He_+ atom is at rest and the hydrogen molecules are carried past it with the velocity of the α particle. The probability of ionization by the component electrons and by the hydrogen nuclei are determined separately. There is still some uncertainty as to the relative primary ionization of electron and of a hydrogen nucleus, so that the calculated results are not as definite as could be wished.

It seems clear, however, that the mean free path for loss is in good general agreement with theory for all velocities of the α particles where observational data are available. It is of interest to note that the agreement of theory with calculation indicates that in most cases the electron captured by an α particle falls rapidly into the lowest quantum orbit and does not appear to circulate in an orbit of high quantum number, *i. e.* of low ionization potential, even for the short interval of time required to traverse the short distance corresponding to the mean free path for loss.

While we can thus offer a quantitative explanation of the observed mean free path for loss of an electron, the inverse problem of the capture of an electron by a swift α particle presents many difficulties. Indeed, it was for a long time implicitly assumed that the α particle could only capture an electron near the end of its range when its velocity was much reduced.

Before considering possible explanations of the phenomena of capture for high-speed α particles, it is desirable to emphasize two important points. We have seen that the

* The α particle often liberates an electron from an atom with sufficient velocity to produce several new pairs of ions. These are included in the term secondary ionization.

† Fowler, Proc. Camb. Phil. Soc. xxi. pp. 21, 532 (1923).

equilibrium between doubly- and singly-charged α particles is very little altered by the nature of the material traversed by the α particle. We know, however, that the ionization per unit path in a gas, and hence the frequency of loss of an electron from He_+, increases rapidly with the mass of the atoms of the gas. Since the frequency of capture is nearly proportional to the frequency of loss over a wide range of atomic weight, it is clear that the fundamental processes involved in capture must be intimately connected with those taking place in the ionization of a gas by an α particle. In a sense, the process of capture is the inverse of the process of ionization where an electron is removed from an atomic system by a passing α particle.

It has been suggested that the process of capture may be connected with the removal of strongly-bound electrons from the nucleus, where a comparatively large amount of energy must be given to the electron to cause its escape from the atom. For example, in nitrogen or oxygen the ionization potential of the K electrons is of the order of 500 volts. While no doubt for low velocities of the α particles the frequency of both capture and loss is to some extent dependent on the strength of the binding of the electron by the nucleus of an atom, there is no evidence that this factor is of importance in the capture of an electron by high-velocity particles. This view is substantiated by the experimental proof that capture occurs readily in hydrogen although its ionization potential is about 16 volts.

In the actual experiments, the α particle is shot at a high speed through molecules which for all practical purposes may be supposed to be at rest. For convenience of discussion, it is sometimes preferable to suppose that the α particle is at rest and the molecules stream by it with a velocity equal and opposite to that of the α particle. We shall first of all consider this hypothetical case of capture of a swift electron by an α particle at rest. The maximum velocity of the α particle from radius C corresponds to a 1040-volt electron—*i. e.*, it is equal to the velocity gained by an electron in falling freely through this difference of potential. For purposes of discussion, it is often very convenient to speak of an electron having a velocity or energy of a 1040-volt electron. Since the ionization potential of the outer electrons of the simple gases varies between 11 and 25 volts, we see that the energy for removal of an outer electron is small compared with that of a 1000-volt electron, and thus cannot seriously influence capture for a swift α particle. On the ordinary theory of a non-radiative

collision between an isolated electron and an α particle, capture can never occur. In practice, however, the electron is always bound to a nucleus, and the collision is not between the isolated charged particles, but involves the interaction of three or more charged systems. In order for capture to occur, the electron must lose in some way the greater part of its energy of translation. It is natural to suppose that this loss of energy occurs by radiation. On such a view, one method of capture of a swift electron by a nucleus may be regarded as the converse of the photo-electric effect in which radiation falls on matter and electrons are ejected. In the case under consideration, swift electrons are shot towards a charged nucleus, and an occasional electron is captured with the emission of its surplus energy in the form of radiation. While it is quite probable that this is one of the processes which lead to the capture of electrons, this conclusion is not of much help in giving us a physical insight into the processes of capture involved in the direct case where a fast α particle collides with an electron in an atom nearly at rest. It is clear that if an electron is captured and moves with the α particle, it must in some way acquire an energy of translation corresponding to that of an electron moving with the velocity of the α particle. For example, capture by a 1000-volt α particle will only be possible if the electron in some way gains energy corresponding to the order of 1000 volts. It is thus natural to suppose that capture is connected with a collision between an α particle and an electron which gives the latter a velocity within a certain range of the velocity of the α particle. If the electron after the collision makes an angle θ with the direction of motion of the α particle, its velocity u is equal to $2V\cos\theta$, where V is the velocity of the α particle. If $u > V$, $\theta < 60°$. It is likely, however, that capture can only occur if the electron ultimately is shot forward within a small angle of the direction of the α particle with a velocity not very different from that of the α particle. Since it is clear that capture does occasionally take place as the result of an encounter of an α particle with a single atom, we are driven to conclude that the interactions of the other charged bodies involved are intimately connected with the mechanism of capture. For example, it is easily seen that the ultimate direction of escape of the electron may depend on a second collision with the nucleus or other electron before escape from the atom. The velocity of the electron is not seriously altered by a nuclear collision, but will always be reduced by a collision with another electron.

Following this line of argument, we can see in a general way that electrons of velocity within a certain range of that of the α particle may occasionally be captured, if their velocity and direction can be altered by a second collision. No doubt the idea of two successive collisions in the atom, each more or less independent of each other, is somewhat artificial. It is much more likely that capture results from what may be regarded as a single encounter between an α particle and two or more charged bodies, and it would prove difficult to separate the factors involved. The whole problem is too involved and complicated to attempt to reduce to calculation, but it may be of interest to give a few estimates of the order of magnitude of the quantities involved.

Suppose an α particle of mass M, charge E, and velocity V collides with an isolated electron of charge e and mass m which is deflected through an angle θ with the original direction of the α particle. With the ordinary notation,

$$p = \mu \tan \theta,$$

where

$$\mu = \frac{Ee}{mV^2}.$$

If the α particle passes through a thickness t of gas containing n electrons per c.c., the number of electrons q which are deflected between the angles 0 and θ is given by

$$q = \pi p^2 . n . t = \pi n t \mu^2 \tan^2 \theta.$$

First, consider the α particles from radium C of velocity $1{\cdot}922 \times 10^9$ cm. per sec. passing through nitrogen at N.P.T. The mean free path for capture is about 3 mm. for this velocity, and

$$\mu = 1{\cdot}37 \times 10^{-10}.$$

Taking 7 electrons per atom,

$$n = 3{\cdot}8 \times 10^{20}, \text{ and for } t = {\cdot}3 \; q = 6{\cdot}7 \tan^2 \theta.$$

Between $\theta = 0$ and $\alpha = 60°$, *i.e.* between velocities 2V and V,

$$q = 20,$$

and p for $60° = 2{\cdot}37 \times 10^{-10}$ cm.

On this calculation, 1 in 20 of the electrons ejected with velocity equal or greater than that of the α particle is captured by it. If an electron can be captured of energy as low as 900 volts, q becomes 28.

For a velocity of α particles $\cdot 47V_0$ (230 volts), the value of mean free path for capture $t = \cdot 037$ mm. For electrons shot out between 0 and 60° for this case $q = 5 \cdot 0$, or one in five collisions is effective in capture. If we suppose the laws of capture hold down to a velocity $\cdot 22V_0$ (50 volts), each collision which gives to an electron more than 50 volts energy results in capture. In this calculation, no correction has been made for the energy required to ionize an atom. No doubt this factor is of importance for such low velocities.

It may be of interest to look at this problem in a somewhat different way. Suppose it be assumed that all electrons are captured that have energies lying between $E+e$ and $E-e$. On the simple collision theory, this is equivalent to the statement that all electrons deflected between angles θ_1 and θ_2 with the direction of the α particles are captured. If E_0 be the energy of an electron moving with the speed of the α particle, then

$$E + e = 4E_0 \cos^2 \theta_1$$

and

$$E - e = 4E_0 \cos^2 \theta_2.$$

The number of collisions which deflect electrons between θ_1 and θ_2 is given by

$$\pi n t \mu^2 (\tan^2 \theta_2 - \tan^2 \theta_1).$$

The value

$$\tan^2 \theta_2 - \tan^2 \theta_1 = \sec^2 \theta_2 - \sec^2 \theta_1$$

$$= \frac{8E_0 e}{E^2 - e^2} = \frac{8e}{E_0}\left(1 + \frac{e^2}{E_0^2} + \ldots\right),$$

if we suppose that the mean value of the energies $E = E_0$ and e/E is small.

If we suppose e to be a constant for all velocities, then since $1/E \propto 1/V^2$ and μ^2 includes the term $1/V^4$, the number of captures per unit path varies as V^{-6}—a deduction in good accord with experiment.

Using the data for capture already given for rays from radium C of maximum velocity 1040 volts, it follows that $e = 19$ volts. On this view the frequency of capture would be in agreement with experiment if all electrons were captured between energies 1021 and 1059 volts. This is equivalent to the assumption that for this speed, only those electrons are captured which are shot within an annular ring of each electron for which the values of p lie between $2 \cdot 40 \times 10^{-10}$ and $2 \cdot 34 \times 10^{-10}$ cm. If it be assumed, as seems probable, that only a fraction of such electrons are

captured, the value of e must be correspondingly increased. If necessary, the formula may be corrected to take account of the energy ω required for ionization. In such a case, E should be replaced by $E_0 + \omega$.

While these calculations give a formal agreement with the results of experiment, they do not offer any definite explanation of the mechanism of capture under the conditions postulated, and in that sense are somewhat artificial. As already pointed out, a collision which results in capture must involve at least three bodies, and is thus not easily amenable to calculation. Under these conditions, it does not appear profitable at this stage to consider the question in more detail. This is all the more so, as in an accompanying paper* Mr. R. H. Fowler has been able to give not only a qualitative, but to a fair approximation a quantitative explanation of the frequency of capture of an electron by an α particle. This is based on certain general deductions from the laws of dissociative equilibrium, which demand that any process such as ionization must be balanced by an analogous reverse process (in this case capture). This must be done in such a way that the rate of the frequencies of the two processes is uniquely determined without any further knowledge of the details of the mechanism, by the condition that the law of dissociative equilibrium must be preserved unaltered.

I desire to express my thanks to my assistant, G. A. Crowe, for his help in these experiments, and to Mr. Ellis, Mr. Blackett, and Mr. Barton for their assistance in counting scintillations.

Cavendish Laboratory,
Dec. 1923.

XXV. *Damped Vibrations.*

By C. F. Jenkin *and* W. N. Thomas †.

In the Phil. Mag. for July 1922 Mr. H. S. Rowell describes a simple method of plotting the damped harmonic motion of a system when the damping force is constant. The figure illustrating his paper is, however, a little misleading, since it corresponds to one of the particular initial displacements which will allow the system to come to rest in the central position. In general the

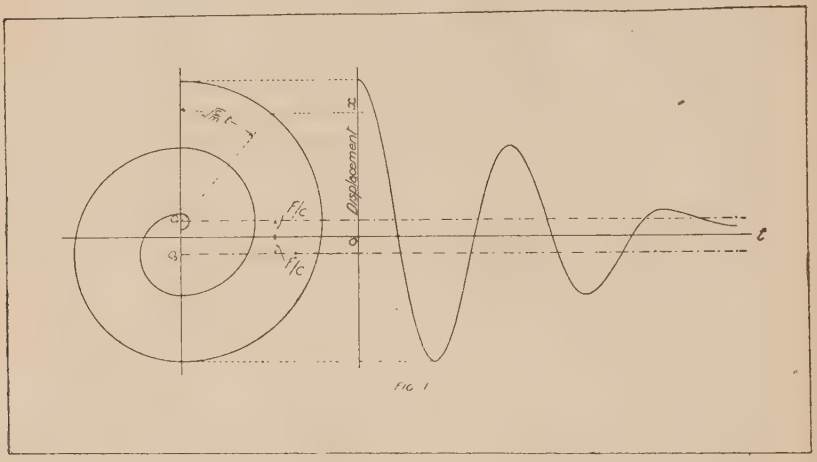
* *Infra*, p. 416.

† Communicated by the Authors.

system may come to rest in any position between the two limiting lines in the diagram. The general case is shown in fig. 1 below. The equation to motion is

$$m\ddot{x} + cx \mp F = 0.$$

Fig. 1.



The solution is (as Mr. Rowell shows)

$$x = A\cos\left(\sqrt{\frac{c}{m}} \cdot t + \epsilon\right) \pm \frac{F}{c},$$

where A is a constant which changes each half period. The value of A for the first half period is (if the initial velocity is zero)

$$A = \text{Initial displacement} - \frac{F}{c}.$$

For the second half period

$$A = \text{Initial displacement} - \frac{3F}{c},$$

and so on. $\epsilon = 0$ if the initial velocity is zero.

The displacement graph is drawn by projection from the series of semicircles drawn round alternate centres O_1, O_2, spaced $\frac{2F}{c}$ apart. The oscillations continue till one of the semicircles finishes within the distance $\pm \frac{F}{c}$ from the central position.

Mr. Rowell's method may be extended to plot the motion when there is both fluid friction (proportional to the velocity) and solid friction (constant).

The equation of motion is

$$m\ddot{x}+b\dot{x}+cx\mp F=0.$$

The solution is

$$x\mp\frac{F}{c}=Ae^{-\frac{b}{m}\frac{t}{2}}\cos(nt-\epsilon),$$

where

$$n=\frac{1}{2}\sqrt{\frac{4c}{m}-\left(\frac{b}{m}\right)^2},$$

and

$$\epsilon=\tan^{-1}\frac{b}{2mn},$$

the initial velocity being assumed to be zero.

A is again a constant, changing each half period. Its initial value is given by

$$A\cos\epsilon=\text{initial displacement}-\frac{F}{c}.$$

Fig. 2.

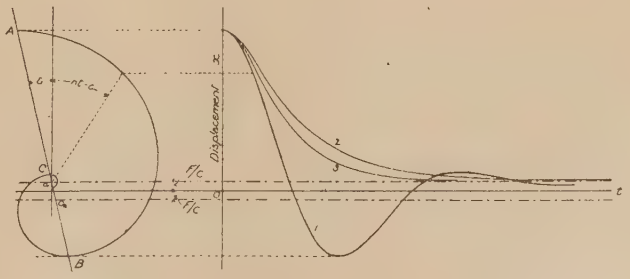


FIG. 2.

The construction of the graph is shown in fig. 2. It is drawn by projection from the series of equiangular spirals AB, BC, etc. drawn round alternate centres O_1, O_2. (These replace the semicircles in Mr. Rowell's case.) The points A, B, C, &c., lie on a sloping line, making an angle $\epsilon=\tan^{-1}\frac{b}{2mn}$ with the axis OX. The tangents to the spirals

at A, B, C, &c., are all horizontal, and the points A, B, C, etc., project into the highest and lowest points in the displacement graph.

The oscillations continue till one of the spirals finishes within the distance $\pm \frac{F}{c}$ from the central position (as before).

If the fluid friction exceeds a certain value

$$\left[i.e.\ \text{if}\ \left(\frac{b}{m}\right)^2 > \frac{4c}{m}\right]$$

the motion ceases to be oscillatory and becomes logarithmic. A logarithmic graph is shown in curve 2, fig. 2. The graph for the critical case $\left[\left(\frac{b}{m}\right)^2 = \frac{4c}{m}\right]$ is shown by curve 3, fig. 2. Neither of these curves presents any difficulty; they are asymptotic to the line $x = \frac{F}{c}$.

XXVI. *The Absence of Ionization by Electrons with Speeds comparable with that of Light.* *By* W. F. G. Swann, *A.R.C.S., D.Sc., Professor of Physics in the University of Chicago* *.

1. *Introduction.*

THE main interest of the problem here discussed lies in its relation to certain types of theories of the earth's electric charge, in which the replenishment of the charge lost by conduction through the atmosphere comes about in virtue of the agency of high-speed electrons shot into the earth from outside. In the earliest form of such theory, proposed tentatively by G. C. Simpson in 1904 †, the electrons come from the sun. In a more recent theory proposed tentatively by the writer they are shot out from the atmosphere as a result of a sort of radioactive disintegration ‡; and, in a still more recent theory proposed by the writer §, and independently by von Schweidler ‖, they are shot out

* Communicated by the Author. Presented at the Christmas meeting of the American Physical Society, 1922.

† "A Theory of the Cause of Atmospheric Electricity," 'Nature,' vol. lxix. p. 270 (1904).

‡ Carnegie Institution of Washington Year Book, 1915.

§ Phys. Rev. vol. ix. pp. 555–557 (1917). Also Journal of the Franklin Institute, vol. clxxxviii. pp. 577–606 (1919).

‖ *Akad. Wiss. Wien. Ber.* vol. cxxvii. 2 *a*, pp. 515–533 (1918).

from the atoms of air through the agency of that so-called penetrating radiation which, supposedly coming from the outer regions of the atmosphere or from some external source, has been invoked for the purpose of accounting for the ionization known to occur in closed vessels freed from radioactive air.

In all such theories the following fundamental difficulty presents itself. The maintenance of the earth's charge necessitates the assumption of an entry of electrons to an extent which amounts, on the average, to 1500 electrons per square centimetre per second. Now, it is a well-known fact that, in the case of electrons travelling with speeds 95 per cent. of that of light, each electron produces about 40 ions in each centimetre of its path ; so that, on this basis, we should expect a rate of production of about 40×1500, *i. e.* 60,000 ions per c.c. per second near the earth's surface, on account of the high-speed electrons ; whereas ions are produced to only one ten-thousandth of this amount, and such ions as are produced may be satisfactorily accounted for by other causes. The object of the present paper is to seek a loophole of escape from this difficulty. The mechanism of the ionization will be discussed in terms of the classical dynamics. This is perhaps a weakness at the present time, when, through the developments of the quantum theory, our ideas as to how a field takes hold of an electron are in such a transitory state ; but, since the quantum theory does not yet speak with completeness on this point, it is perhaps not out of place to derive some comfort from showing that even the classical theory may be made to indicate an avenue of escape from the difficulties presented by the large ionization which a superficial view of the situation would suggest as a result of the influx of high-speed electrons to the earth. In what follows, the discussion of fine points, and mathematical details, will be relegated to an appendix at the end of the paper.

2. *Preliminary Formulation of the Theory.*

Suppose that an electron is situated within an atom, and that another electron of high speed, which we shall distinguish by calling it a corpuscle, passes near to the electron. As the corpuscle describes its orbit it will communicate energy to the electron, and will eject it from the atom if the energy communicated is sufficient. Such a theory of ionization was suggested originally by Sir J. J. Thomson *, and was later elaborated by N. Bohr †. The

* Phil. Mag. ser. 6, vol. xxiii. pp. 449–457 (1912).
† Phil. Mag. ser. 6, vol. xxx. pp. 581–612 (1915).

greater the velocity of the corpuscle, the shorter the time during which the electron has opportunity to receive momentum from it; so that the efficiency of the corpuscle as regards its power to hurl the electron out of the atom diminishes with its velocity, and would, as a matter of fact, become zero if the corpuscle could attain an infinite velocity. The velocity of the corpuscle cannot attain a value greater than that of light, however; so that, as regards this effect, there is not very much reduction in ionizing efficiency from, say, 95 per cent. of the velocity of light, where the ionization has been measured, to the velocity of light itself *. As the velocity of light is approached, however, another phenomenon comes in. The field of the corpuscle does not remain uniformly distributed, but, in accordance with ordinary electrodynamical principles, it crowds up more and more towards the equatorial plane of the corpuscle's motion. The time which the corpuscle has for acting effectively on the electron is therefore reduced still further on this account, but the intensity of the field during that time is correspondingly increased; and it turns out, as has been shown by N. Bohr †, that if we take nothing else into consideration, the energy communicated to a free electron by

* The simple theory gives the ionization per centimetre of path as inversely proportional to mV^2, where V is the velocity of the corpuscle and m the electronic mass. For slow velocities, $\frac{1}{2}mV^2$ is the kinetic energy, so that the statement is made that the ionization per centimetre of path is inversely proportional to the kinetic energy. Von Schweidler (*Akad. Wiss. Wien Ber.* vol. cxxvii. 2 *a*, pp. 515–533, 1918), taking this statement, substitutes for $\frac{1}{2}mV^2$ the relativity expression

$$m_0c^2\left\{\left(1-\frac{V^2}{c^2}\right)^{-\frac{1}{2}}-1\right\}$$

for the kinetic energy, which becomes infinite as V approaches c, the velocity of light. He thus concludes that the ionization should diminish indefinitely as the velocity of the corpuscle approaches that of light. It would appear, however, that the conclusion cannot be substantiated on this basis; for a detailed examination of the elements of the calculation will show that the $\frac{1}{2}mV^2$ occurs in the original expression not really as the representative of the kinetic energy of the corpuscle, nor of anything which should attain an infinite value as V approaches the velocity of light. Indeed, the m in that expression is really the representative of the mass of the electron which is *being ejected* from the atom, while the V is the velocity of the corpuscle. The occurrence of V^2 in the denominator of the expression for the ionization per centimetre of path is closely bound up with the fact that the time during which the corpuscle is in effective proximity to the atom diminishes with the velocity. A fuller analysis of the situation is given in Appendix, Note 1.

† Phil. Mag. ser. 6, vol. xxx. pp. 581–612 (1915). See also Appendix, Note 1.

the passage of the corpuscle will be unaffected by this concentration of the lines of force towards the equatorial plane *.

There is, however, one very important consideration which must be taken into account. The impartation of even a small amount of energy to an electron in a very short time results in a large radiation of energy. In fact, if the velocity of an electron increases with acceleration f, the rate of radiation is proportional to f^2 †. If, then, f is infinite, while $\int f\,dt$, the velocity gained, is finite, it is obvious that $\int f^2\,dt$ will be infinite. Now, the nearer the velocity of the corpuscle approaches the velocity of light, the more suddenly does the corpuscle communicate to the electron such energy as it imparts; and, as will be shown in greater detail below, the situation is such as is approximately symbolized by the following:—In the case of a corpuscle moving with a velocity approximating that of light (say 95 per cent. of that of light), but not so closely as to involve radiation considerations, it turns out, as may readily be shown from Sir J. J. Thomson's theory, that the corpuscle must approach an electron of an oxygen atom within $0{\cdot}7 \times 10^{-10}$ cm. in order to give to that electron enough energy to insure its ejection from the atom—an energy corresponding to the fall of the electronic charge through 15·5 volts. If the minimum distance of approach is less than this amount, the energy imparted to the electron will be greater; if it is more, the energy imparted will be less. It is, however, possible to assign to the corpuscle a velocity so high that, *irrespective of the distance of approach*, if we should suppose it to transmit to the electron an energy corresponding to 15·5 volts, we should lead ourselves to the impossible conclusion that the electron's acceleration would be so large that the energy *radiated* by it in acquiring its velocity would be greater than the work done on it by the corpuscle. Thus, corpuscles having the velocity in question, or any higher velocity, would be unable to eject an electron from the atom of oxygen.

* When the electron is bound in the atom, the considerations are modified, as shown by Bohr's calculations; but a situation such as that under discussion, where the time of action of the force on the electron is exceptionally short, is, of all cases, the one most favourably adapted to the neglect of binding forces on the electron.

† For very rapid changes of acceleration, this statement involves assumptions which are discussed in Appendix, Note 2.

3. *Mathematical Formulation of the Problem.*

For the corpuscular speeds concerned, where the mass is so many times the mass for small velocities, the corpuscle will suffer but little deviation in passing the electron, and it will suffice to regard its path as straight for the purpose of calculating the force which it exerts upon the electron as a function of the time. Moreover, in calculating this force, we shall regard the electron as a *point* charge. The latter assumption presents certain difficulties concerned with the variation of the field of the corpuscle over the volume of the electron and with the inertial and radiation reactions. A discussion of these is given in Appendix, Note 2.

According to the classical electrodynamics, an electron of charge e, moving with acceleration f, radiates energy at a rate $2e^2f^2/3c^3$, where c is the velocity of light.

If F is the force on the electron at any instant, v its velocity at that instant, and v_0 the maximum velocity which it attains, we always have

$$v_0\mathrm{F} \geqslant v\mathrm{F} > \frac{2e^2f^2}{3c^3}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

since the rate of doing work by the external force on the electron must always be greater than the rate of radiation of energy by the electron in a case like that under consideration, where the velocity increases continually with the time. Thus

$$f < \left(\frac{3c^3v_0}{2e^2}\right)^{\frac{1}{2}} \mathrm{F}^{\frac{1}{2}}$$

and

$$v_0 < \left(\frac{3c^3v_0}{2e^2}\right)^{\frac{1}{2}} \int_0^\infty \mathrm{F}^{\frac{1}{2}}\,dt.$$

Putting $dx = c\,dt$, with the path of the corpuscle as the axis of x, and the origin at the point of nearest approach, we have

$$v_0^{\frac{1}{2}} < \left(\frac{3c}{2e^2}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} \mathrm{F}^{\frac{1}{2}}\,dx.$$

Hence,

$$\tfrac{1}{2}mv_0^2 < \frac{9}{8}\frac{mc^2}{e^4}\left[\int_{-\infty}^{\infty} \mathrm{F}^{\frac{1}{2}}\,dx\right]^4.$$

Now, if p is the distance of nearest approach, the force on the electron due to the corpuscle is *

$$\mathrm{F} = \frac{e^2(1-\beta^2)^{-\frac{1}{2}}p}{[(1-\beta^2)^{-1}x^2+p^2]^{\frac{3}{2}}}.$$

* See, for example, O. W. Richardson, 'The Electron Theory of atter,' p. 249.

Hence, putting $(1-\beta^2)^{-\frac{1}{2}}x/p=\alpha$, we readily find

$$\int_{-\infty}^{\infty} \mathrm{F}^{\frac{1}{2}}\,dx = e(1-\beta^2)^{\frac{1}{4}}\int_{-\infty}^{\infty}\frac{d\alpha}{(1+\alpha^2)^{\frac{3}{4}}}$$

and

$$\tfrac{1}{2}mv_0^2 < \frac{9}{8}(1-\beta^2)mc^2\left[\int_{-\infty}^{\infty}\frac{d\alpha}{(1+\alpha^2)^{\frac{3}{4}}}\right]^4,$$

or, since the integral is an even function of α,

$$\tfrac{1}{2}mv_0^2 < \frac{9}{4}(1-\beta^2)mc^2\left[\int_{0}^{\infty}\frac{d\alpha}{(1+\alpha^2)^{\frac{3}{4}}}\right]^4.$$

Putting $\alpha=\tan\theta$, we readily find

$$\tfrac{1}{2}mv_0^2 < \frac{9}{4}mc^2(1-\beta^2)\left[\int_0^{\frac{\pi}{2}}\frac{d\theta}{\sqrt{\cos\theta}}\right]^4. \quad . \quad . \quad (2)$$

The integral is known * to be equal to $\sqrt{2}\,\mathrm{K}\left(\frac{1}{\sqrt{2}}\right)$, where K is the elliptic integral

$$\mathrm{K} = \int_0^{\frac{\pi}{2}}\frac{d\phi}{\sqrt{1-\frac{1}{2}\sin^2\phi}},$$

and is found, from tables, to be equal to 1·854. Thus we find

$$\tfrac{1}{2}mv_0^2 < 106\,(1-\beta^2)mc^2. \quad . \quad . \quad . \quad . \quad (3)$$

If W is the ionization potential of the atom containing the electron, the energy which must be imparted to the latter to enable it to escape is We, so that ionization will not occur if

$$\mathrm{W}e \geq 106\,(1-\beta^2)mc^2,$$

and the highest value of β which will result in ionization is given by

$$1-\beta^2 = \frac{\mathrm{W}e}{106\,mc^2}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Taking W as corresponding to 15·5 volts † (0·0517 e.s.u.) for oxygen, we find $1-\beta^2=2{\cdot}98\times10^{-7}$, which corresponds to $c-\mathrm{V}=45$ metres per second, where V is the velocity of the corpuscle. The conclusion is that a corpuscle moving with a velocity equal to or greater than that corresponding to 45 metres per second less than the velocity of light would be unable to eject an electron from an atom of oxygen, the

* See D. Bierens de Haan, *Tables d'Intégrales Définies*, p. 125.

† See Foote and Mohler, 'The Origin of Spectra,' p. 67.

most easily ionized constituent of the principal gases of the atmosphere. It will, of course, be understood that the value calculated for V merely represents a value which is certainly greater than that at which ionization ceases.

In spite of the very close approximation of the above velocity to that of light, the value 45 metres per second less than the velocity of light happens to be exactly the velocity which Birkeland has found it necessary to assign to solar electrons if the bending which these electrons suffer in the earth's magnetic field is to be consistent with their accounting for the aurora *. Electrons of lower speeds would suffer too large deviations in the field to permit of their accounting for the facts. The diminution of bending resulting from approximation of the velocity to that of light, results not so much from the direct influence of high speed, as from the increase in the mass of the electron which approximation to the velocity of light implies. It is, of course, a fact that, if the present theory were true, it would lead to the conclusion that Birkeland's corpuscles could not ionize at all, so that they could not well account for the aurora; but it is now generally believed that the aurora is not caused by negative electrons, and the comparison with Birkeland's conclusions is only cited to show that, in invoking speeds only 45 metres per second below that of light, one would not be doing anything more drastic than has been already done in other branches of the subject. It may perhaps be worth while pointing out that closeness of approximation to the conditions pertaining to the velocity of light is not well symbolized by closeness of approximation of V to c; for, as regards the energy of a corpuscle, for example, there is an infinite range from that corresponding to V less than c by 45 metres per second, and $V=c$.

As a special aspect of the above comparison with Birkeland's data, it may be of interest to point out that, if an electron were shot from infinity into our atmosphere—in the equatorial plane, for example,—it would not reach the earth, but would be turned back into space by the earth's magnetic field unless it had a velocity nearer to that of light than the velocity which we have calculated as sufficiently great to insure absence of ionization. Indeed, with this velocity (45 metres per second below the velocity of light) the corpuscle would not succeed in approaching nearer to the earth than about 8 times the earth's radius. (See Appendix, Note 3.)

* See K. Birkeland, 'The Norwegian Aurora Polaris Expedition, 1902–3,' vol. i. Section 2, p. 596.

4. *Absorption of the Corpuscles by the Atmosphere.*

N. Bohr has worked out a theory for the decrease of velocity of swiftly moving electrified particles in passing through matter *, and has given an expression for the range of such corpuscles. The assumptions of Bohr's theory are such as to render very doubtful the application of the theory to ranges such as those with which we are concerned in the case of the high energy corpuscles under discussion, quite apart from the radiation reactions which we have invoked. If, however, as a matter of general interest, we merely take Bohr's formula and apply it to the present case, we find that for particles with velocity as near to that of light as .45 metres per second, it gives a range certainly more than two kilometres at atmospheric pressure (see Appendix, Note 4). Bearing in mind that the very mechanism by which the corpuscles lose energy on Bohr's theory (the impartation of energy to electrons by which they pass) is denied them, or at any rate greatly curtailed, by the radiation reaction considered in the present paper, we see that there is no obvious difficulty in assuming ranges considerably greater than two kilometres at atmospheric pressure.

It would thus appear that *there is mutual consistency between the phenomena in the statement that if corpuscles should enter our atmosphere from outside, in the equatorial plane, with energies sufficient to enable them to reach the earth's surface in spite of the earth's magnetic field, which would tend to return them to space, they would pass right through our atmosphere with but little absorption, and would fail to ionize the air through which they passed.*

In considering a complete theory of absorption along the lines suggested by the foregoing, it would, of course, be necessary to take into account the energy imparted to the atomic nuclei. The radiation considerations do not operate as forcefully in the case of the nucleus as in that of the electron. However, the amount of energy imparted for a given distance of approach is less in the case of the nucleus than in that of the electron, as may be seen from (7) (Appendix, Note 1) by replacing two of the electronic charges in that formula by nuclear charges, and the electronic mass m_2 by the nuclear mass. In any case, a theory of absorption, even with neglect of radiation considerations, involves complicated considerations which cannot be adequately discussed briefly †, and is not one of the objects of this paper.

* Phil. Mag. ser. 6, vol. xxx. pp. 581–612 (1915).

† N. Bohr, *loc. cit.*

Appendix.

Note 1. *Concerning the form assumed by Sir J. J. Thomson's theory of ionization when the speed of the corpuscle approximates to that of light.*

Quite apart from all other considerations, it is, of course, not permissible to take the results which have been calculated on the assumption of low velocities and replace the final quantities which occur therein by the expressions which the theory of relativity would assign to those quantities. The proper procedure is to apply the relativity considerations at the beginning of the derivation.

If the corpuscle travels along the axis of x with the origin at the point of nearest approach, and if p is the nearest distance of approach and β the ratio of the velocity of the corpuscle to that of light, the force F on the electron resolved in a direction perpendicular to the x-axis is

$$\mathrm{F} = e^2 \frac{(1-\beta^2)^{-\frac{1}{2}} p}{[(1-\beta^2)^{-1}x^2 + p^2]^{\frac{3}{2}}}. \quad . \quad . \quad . \quad . \quad (5)$$

This neglects the effect of variation of the corpuscle's field over the region occupied by the electron itself, a point which is not concerned in our discussion of von Schweidler's conclusion, however.

As explained in Section 3, in the case of corpuscular velocities nearly equal to that of light, it is sufficient to assume that the path of the corpuscle is straight, and to consider only the influence of the above component of the force in calculating the momentum given to the electron. The total momentum given to the electron by the corpuscle of velocity V is,

$$\mathrm{M} = \int_0^\infty \mathrm{F}\, dt = \frac{1}{\mathrm{V}} \int_{-\infty}^{\infty} \mathrm{F}\, dx = \frac{e^2}{\mathrm{V}} \int_{-\infty}^{\infty} \frac{(1-\beta^2)^{-\frac{1}{2}} p\, dx}{[(1-\beta^2)^{-1}x^2 + p^2)]^{\frac{3}{2}}}.$$

On making the transformation $(1-\beta^2)^{-\frac{1}{2}} x/p = \tan\theta$, the integral becomes readily evaluated, and we find

$$\mathrm{M} = \frac{2e^2}{p\mathrm{V}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If m_2 is the mass of the electron in the atom, the velocity attained is M/m_2, and the kinetic energy gained is

$$\mathrm{Q} = \tfrac{1}{2} m_2 \left(\frac{\mathrm{M}}{m_2}\right)^2 = \frac{2e^4}{m_2 \mathrm{V}^2 p^2}; \quad . \quad . \quad . \quad . \quad (7)$$

showing, as stated in the footnote on p. 308 (Section 2), that the

m in the denominator is really the mass of the electron, and not that of the corpuscle. Following J. J. Thomson's theory, the ionization for one centimetre of the path is proportional to $1/m_2V^2$.

Equation (7) happens to be exactly the same as the expression resulting from Sir J. J. Thomson's theory for low corpuscular velocities. Thus, the theory in question results in

$$Q = \frac{4T\gamma^2}{m_1 m_2} \frac{1}{\left[1 + \frac{p^2 V^4 \gamma^2}{e^4}\right]}, \quad . \quad . \quad . \quad . \quad (8)$$

where T is the kinetic energy and m_1 the mass of the corpuscle, while γ is written for $m_1 m_2/(m_1 + m_2)$. For all cases of interest, the denominator under the square bracket in (8) is large compared with unity, so that, replacing T by $\frac{1}{2}m_1V^2$ for low velocities,

$$Q = \frac{2e^4}{m_2 V^2 p^2},$$

which is the same as (7) ; and, by retaining the subscript 2 in the mass, exhibits this quantity in its true form as the mass of the electron which receives the energy rather than the mass of the corpuscle which imparts the energy.

NOTE 2. *Regarding considerations arising from the finite size of the electron.*

In Section 3 it is implied that the suddenness with which the electron gains such velocity as it acquires increases indefinitely as the speed of the corpuscle approaches that of light, our basis for this assumption being the fact that the field of the corpuscle becomes infinitely contracted towards the equatorial plane of the motion as the velocity of light is approached. The truth of this is only certain when the electron is a point. A finite size for the electron would presumably insure that its gain of velocity was extended over a period at least as great as the time taken by the corpuscle in travelling a distance equal to the electronic diameter, so that increase of the velocity of the corpuscle beyond a certain point would become ineffective in limiting, through further enhancement of the radiation considerations, the energy transmitted to the electron. Moreover, according to strict classical theory, electrons of *finite* radius radiate only finite amounts of energy for infinitely rapid changes from one constant velocity to another, as P. Hertz has shown (*Inaugural-Dissertation*,

Göttingen, 1904) and a corpuscular velocity equal to that of light would not, on strict classical theory, necessarily prevent ionization for electrons of radius $1{\cdot}8\times10^{-13}$ cm. For infinitesimal electrons the customary expression for radiation is correct.

The origin of the idea of a finite size for the electron is to be found in the fundamental law from which the motion of the electron is usually determined—the law that the electron moves, at each instant, in such a manner that its reaction on itself due to its motion is equal to the force due to the external field integrated over it. In the practical utilization of this law the electron is assumed to be a shell of charge, uniformly distributed over the surface of a sphere when the electron is at rest, and contracted into an ellipsoid when it is in motion, in a manner determined by the requirements of the theory of relativity. When one examines the origin of this law, one cannot avoid being impressed by its artificiality. At the best it seems but a rather crude attempt to go one stage beyond the mere acceptance of a relation between the time derivatives of the motion of the electron and the external force as an empirical fact. It becomes particularly doubtful in a case such as that under discussion, where the field due to the corpuscle varies appreciably over the volume of the electron whose motion is being studied; for it makes no attempt to allow for any dependence of the electronic charge distribution on the variableness of this external field. One who takes this picture of the law of motion as fundamental will, of course, be driven to assume a finite size for the electronic sphere as a result of association of the experimentally measured mass with the quantity which the law assigns to that position. In view of the weaknesses of the law, it would seem not illogical to refuse to be too tightly bound by it if it should turn out convenient to regard the electron as a point in considering its radiation and the action of the external field upon it. On this basis the mass appears simply as a coefficient which relates the acceleration of the electron to the external field; but sacrifice of its complete electrodynamic origin does not prevent our permitting it to vary with velocity in a manner demanded by relativity. In adopting such a procedure, we must be careful that we do not commit a breach of logic by retaining the expression $2e^2f^2/3c^3$ for the rate of radiation of energy by the electron. A consideration of the origin of this expression shows, however, that the assumption concerned is not involved so fundamentally in it as in the matter of the mass; and the expression may still be regarded as retaining

a meaning, even though we discard the electrodynamic origin of mass in the sense ordinarily understood, provided that we still retain the customary expressions for the electromagnetic energy density in the field *. A full discussion of the fine points of this matter would form an article in itself, and would be out of place here. It is fully admitted that a departure from the strict standpoint of classical electrodynamics is made in regarding the electron as a point for the purpose of considering the action of the external field on it; but in making this assumption for the purpose of alleviating the difficulty presented by corpuscular ionization, which matter it is the object of this paper to discuss, we at least replace that very obvious and vital difficulty by one which is concerned with the rather fine points of electrodynamics, and which exists there only when we retain a strict adherence to a form of the law of electronic motion which is itself probably inexact.

NOTE 3. *Concerning the path of a corpuscle entering the atmosphere in the equatorial plane of the earth's magnetic field.*

Imagine an electron projected from infinity along a radius vector directed initially towards the centre of the earth, and lying in the plane of the equator. The magnetic field does no work on the electron, since it acts at all points in a direction perpendicular to the line of flight. As a consequence, the resultant velocity of the electron does not change.

If m is the transverse electromagnetic mass, and ρ the radius of curvature at any point of the path, we have, in electromagnetic units,

$$\frac{m\mathrm{V}^2}{\rho} = \mathrm{H}e\mathrm{V}.$$

Putting $\mathrm{H} = \mathrm{M}/r^3$, where M is the moment of the earth, we find,

$$\rho = \frac{m\mathrm{V}r^3}{e\mathrm{M}}.$$

But, if p is the perpendicular distance from the origin, the

* A discussion of some of the points concerned in the relation between the law of electronic motion on the one hand, and electromagnetic mass and energy on the other, will be found in "Fundamentals of Electrodynamics," pp. 33-44, Part 1 of the National Research Council's report on Electrodynamics of Moving Media.

origin being on the convex side of the curve, and the radius of curvature being regarded as positive, we have

$$\rho = -r\frac{dr}{dp}.$$

Hence

$$-\frac{dr}{dp} = \frac{m\mathrm{V}r^2}{e\mathrm{M}}$$

and

$$p = \frac{\mathrm{M}e}{mvr}.$$

The constant of integration is zero, since $p=0$ at $r=\infty$.

The smallest value of r is obtained by putting $r=p$, which corresponds to the lowest point of the orbit. Thus, measured from the earth's centre, the lowest altitude attained is

$$\text{Minimum altitude} = \left(\frac{\mathrm{M}e}{m\mathrm{V}}\right)^{\frac{1}{2}} = \left\{\frac{\mathrm{M}e(1-\beta^2)^{\frac{1}{2}}}{m_0\mathrm{V}}\right\}^{\frac{1}{2}},$$

where m_0 is the mass for small velocities. Inserting $1-\beta^2=2{\cdot}98\times10^{-7}$, as given in Section 3, and putting $e/m=1{\cdot}77\times10^{7}$ e.m.u., $\mathrm{V}=c$, and $\mathrm{M}=0{\cdot}9\times10^{26}$ e.m.u., we find $p=5{\cdot}4\times10^{9}$ cm.

Note 4. *Concerning conclusions to be drawn from N. Bohr's theory of the "Decrease of Velocity of Swiftly Moving Electrified Particles in passing through Matter"* (Phil. Mag. ser. 6, vol. xxx. pp. 581–612, 1915).

For the range of a corpuscle, Bohr gives in his equation (28) the following expression:

$$\mathrm{R} = \frac{m^2c^4}{2\pi e^4\mathrm{N}\Sigma}\left[(1-\beta^2)^{\frac{1}{2}} + (1-\beta^2)^{-\frac{1}{2}} - 2\right], \quad . \quad (9)$$

where Σ is given by his equation (27) as

$$\Sigma = \sum_1^n \left[\log\frac{k^2c^2\mathrm{N}n\Delta x}{4\pi\nu^2} - \log\left(\frac{1-\beta^2}{\beta^2}\right) - \beta^2\right]. \quad . \quad (10)$$

In these expressions, N is the number of atoms per c.c., n the number of electrons in an atom, ν a frequency characteristic of the atom and taken by Bohr as given by $\left(\Sigma_1^n \log\nu\right)/n = 38{\cdot}3$ for air (see p. 597 of his paper). The quantity Δx has a rather complicated meaning for which reference must be made to the original paper. However, it will be seen that its value cannot be comparable

with, or at any rate greater than, the whole range R. If, then, we replace it by R in the equations (9) and (10) above, we shall certainly calculate a value of R which is too small. Moreover, it may be noted that the approximation made by Bohr in treating Σ as a constant during the integration by which he obtains his equation (28) is such as to reduce further the calculated value of R. Of course, the nature of the assumptions in Bohr's theory are such as to render its application to ranges such as we are considering very doubtful. If, however, merely as a matter of general interest we calculate the value of R on the above lines, with Δx replaced by R, and with the value $1-\beta^2=2{\cdot}98\times10^{-7}$ corresponding to the corpuscles we have discussed in Section 3, we find, on using Bohr's data for ν, n, k, etc.,

$$R = 2{\cdot}2\times10^{5} \text{ cm.}$$

Ryerson Physical Laboratory,
University of Chicago,
October 10, 1923.

XXVII. *On the Secondary Failure of Thin Tubes of Circular Section subjected to Terminal Couples.* *By* M. S. Ahmed *.

1. IT is well known that cylindrical tubes are liable to secondary failure, if they are sufficiently thin, when subjected to end compression †, as in aircraft construction, or to external pressure as in boiler tubes ‡. When thin cylindrical tubes are subjected to terminal couples, their circular sections distort into ovals, and the stresses produced by the change of shape may cause breakdown before the ordinary primary stresses, parallel to the axis, would cause it.

The following investigation is to determine under what conditions the secondary stresses due to deformation of the cross-section into an oval shape exceed the primary stresses found on the ordinary Theory of Pure Bending.

Some possible applications are :—

A monocoque fuselage of an aeroplane which has hitherto been usually built of wood, and might perhaps in the future be made of metal, can possibly be regarded, to a first

* Communicated by Mr. R. V. Southwell, M.A.

† Southwell, "On the General Theory of Elastic Stability," Phil. Trans. Roy. Soc. 1913.

‡ Love, 'Theory of Elasticity,' 3rd edition, Chapter 24 A; Southwell, Phil. Mag. 1913 and 1915.

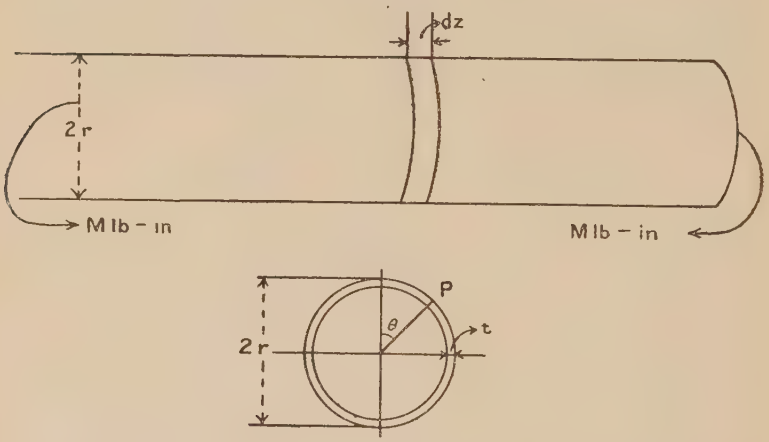
approximation, as a cylinder, bent by wind loads on the tail structure.

A steel factory chimney under wind load is another example.

A somewhat similar stress system possibly arises in a racing eight, or a submarine, under action of the rudder.

The conclusion is that secondary stresses are not likely to be important in steel construction, but are likely to matter in wood ; stiffening rings are then required to compensate.

Fig. 1.



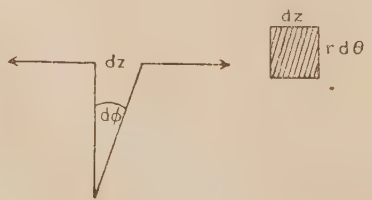
According to the theory of bending, $\frac{f}{y}=\frac{M}{I}=\frac{E}{R}$, where f, y, M, I, &c., have their usual significance (fig. 1),

$$I=\pi r^3 t,$$

$$R=\frac{E\pi r^3 t}{M},$$

at P, f (tensile) $= M\cos\theta/\pi r^2 t$.

Fig. 2.



On an elementary volume $r\,d\theta\,dz\,t$ (fig. 2) there are

tensions

$$\frac{\mathrm{M}\cos\theta}{\pi r^2 t}\,.\,r\,.\,d\theta\,.\,t \text{ lb.}$$

at angle $d\phi$, where $\mathrm{R}\,d\phi = dz$.

These have a resultant vertically downwards of amount

$$\frac{\mathrm{M}\cos\theta}{\pi r^2 t}\,.\,r\,d\theta\,\frac{dz}{\mathrm{R}}\,t\ ;$$

i. e., resultant radial pressure

$$\frac{\mathrm{M}\cos\theta}{\pi r^2 t}\,.\,tr\,d\theta\,\frac{dz}{\mathrm{R}}\cos\theta \text{ on area } r\,d\theta\,dz\ ;$$

i. e.,

$$\frac{\mathrm{M}t\cos^2\theta}{\pi r^2 t\mathrm{R}} = \frac{\mathrm{M}^2\cos^2\theta}{\mathrm{E}\pi^2 r^5 t} \text{ per unit area}$$

$$= \frac{\mathrm{E}r\cos^2\theta t}{\mathrm{R}^2} \text{ lb. per square inch.}$$

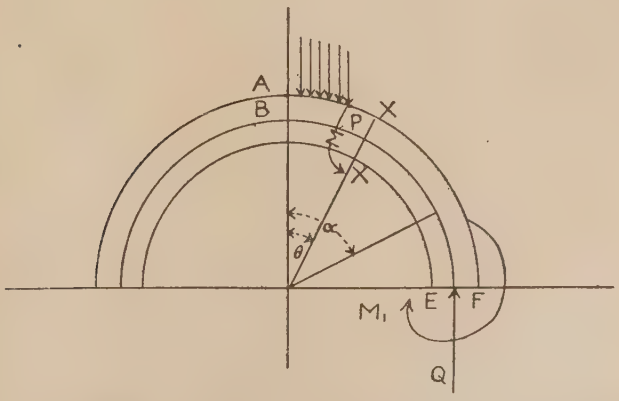
Call

$$\frac{\mathrm{E}rt}{\mathrm{R}^2} = p, \text{ say ;}$$

i. e., external radial pressure on the cylinder

$$= p\cos^2\theta \text{ lb. per square inch.}$$

Fig. 3.



Let us consider the case of a ring of breadth C subjected to external loading $p\cos\theta$ lb. per square inch vertically downwards (fig. 3). The thrust Q on EF

$$= \int_0^{\pi/2} p\cos\theta\,.\,c\,.\,r\,d\theta = pcr.$$

Take moments about XX for equilibrium of the portion XXEF,

$$M = M_1 - Q(r)(1-\sin\theta) + \int_{\theta=\alpha}^{\theta=\pi/2} p\cos\alpha \,.\, cr\,d\alpha \,.\, r(\sin\alpha - \sin\theta)$$
$$= M_1 - \tfrac{1}{2}pcr^2\cos^2\theta.$$

From the symmetry of the deformation, it follows that the integrated bending moment from A to F = 0. Hence

$$\int_{\theta=0}^{\theta=\pi/2} di = \int_0^{\pi/2} \frac{M}{EI} r\,d\theta = \frac{r}{EI}\int_0^{\pi/2} (M_1 - \tfrac{1}{2}pcr^2\cos^2\theta)d\theta,$$

so that

$$M_1 = \tfrac{1}{4}pcr^2, \quad \text{and} \quad M = -\tfrac{1}{4}pcr^2\cos 2\theta.$$

M vanishes when $\theta = 45°$.

Maximum $M = (1/4)\,pcr^2$ at top or sides, and this produces a maximum stress of amount

$$\frac{3}{2}\frac{pr^2}{t^2} \text{ lb. per square inch.}$$

But

$$p = \frac{Ert}{R^2} = \frac{M^2}{E\pi^2 r^5 t},$$

and therefore maximum stress

$$= \frac{3}{2\pi^2}\frac{M_2^2}{Er^3t^3} \text{ lb. per square inch.} \quad . \quad . \quad (1)$$

Compare this with the primary maximum stress

$$f = \frac{M_1}{\pi r^2 t}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

For example, take a mild steel tube where

$t = \cdot 028$ in.,

$r = 1$ in.,

$E = 30 \times 10^6$ lb. per square inch,

and take maximum stress = 45,000 lb. per square inch, and find M in the two cases :—

From (2):

$$M_1 = 45{,}000 \times \frac{22}{7} \times 1 \times \cdot 028 = 3970 \text{ lb. inches}$$ is the bending moment that would cause failure by primary stress.

From (1):

$$M_2^2 = 45{,}000 \times \frac{2\pi^2}{3} \times 30 \times 10^6 (\cdot 028)^3$$

or $M_2 = 14{,}000$ lb. inches is the bending moment that would cause failure by *secondary* stress ; *i. e.*, for aeroplane tubes, ordinary primary stressing is always all right.

As another example, consider a wooden monocoque fuselage, diameter 100 inches and thickness 1/8 inch :

$$\left.\begin{aligned} E &= 1{\cdot}3 \times 10^6 \\ f &= 5000 \end{aligned}\right\}$$ lb. per square inch approximately.

From (2):

$$M_1 = f\pi r^2 t$$
$$= 5000 \times \pi \times 2500 \times 1/8 = 4{\cdot}9 \times 10^6 \text{ lb. in.}$$

From (1):

$$M_2^2 = \frac{2}{3} \times \pi^2 \times f \times E \times r^3 \times t^3$$
$$= 5000 \times \frac{2}{3} \times 1{\cdot}3 \times 10^6 \times 125{,}000 \times \frac{1}{512}$$

or $M_2 = 3{\cdot}24 \times 10^6$ lb. in.

Hence in this case failure is due mainly to secondary, not primary stresses ; and primary stressing would overestimate the factor of safety by 50 per cent. To compensate the effect considered stiffening rings are generally inserted.

XXVIII. *Heat Dissipation from the Surfaces of Pipes and Cylinders in an Air Current.* *By* Professor A. H. Gibson, *D.Sc.**

(1) THE following experiments were carried out primarily with a view of obtaining data as to the rate of heat dissipation from tubular metal surfaces adaptable as oil coolers for aircraft. For this purpose a series of tubes of different materials and having different surface coatings were used, made up into spiral coils. The experiments were afterwards extended so as to obtain the relationship between the heat dissipated per unit length of a given pipe when forming part of such a coil, and when exposed normally to the direction of the air current. Also, in order to determine the magnitude of the dimensional effect, a series of experiments were carried out on a straight pipe of considerably larger diameter. A comparison is made between these results and those obtained by Hughes † on a series of copper pipes covering approximately the same range of diameters.

(2) *Apparatus.*—The experiments were carried out in a 6 ft. × 4 ft. wind tunnel at the Royal Aircraft Establishment, Farnborough. For the tests a number of thin, cold drawn pipes were formed into spiral coils, each 8 inches in diameter and 2 ins. pitch. The length in each case was 12 feet. Each coil was mounted in the wind tunnel with its axis vertical. Hot water was circulated through the coil, the inlet and outlet temperatures and the quantity being carefully measured. In the majority of the tests the temperature of the inlet water was 95° C., and the mean temperature approximately 90° C. Tests were, however, carried out with inlet temperatures as low as 30° C. in order to obtain the rate of variation of heat dissipation with temperature difference. The air temperature throughout the experiments was approximately 12° C. All these temperatures were accurately measured.

The temperature of the inlet and outlet water was measured by calibrated mercury thermometers, capable of reading to ·01° C., fitted into enlargements of the supply and discharge pipes, immediately before and after their connexion to the pipe coil. The connexion between the pipe coil and the supply and discharge pipes was made by rubber junctions. In order to eliminate any end effects and the effect of loss of heat between the thermometers and the

* Communicated by the Author.

† Phil. Mag. vol. xxxi. p. 188 (1916).

experimental pipe, the latter was removed and replaced by a short length (3 ins.) of heavily lagged piping. The difference of readings of the two thermometers at the same mean temperatures and air velocities as in the normal tests was then measured, and this has been deducted from the difference observed in the latter tests.

The flow of water through the pipes ranged from 4 to 7 lb. per minute, and experiments show that over this range the velocity of flow has no appreciable effect on the heat dissipation from the outer surface, so long as the mean temperature remains constant. This can only be the case if the mean temperature of the inner surface is sensibly the same as that of the water, and the assumption has been made in all the tests that this is the case whenever a further increase in the rate of water flow, at a given air speed, is not accompanied by an increase in heat loss from the cooling surface.

Since this is a vital assumption it was decided to check it experimentally, and with this in view two series of tests were carried out on one of the coils. In one series, the heat was supplied by the circulating water. In the other, the heat was supplied by a heavy low-voltage current passing through the coil as a resistance. This was adjusted until the inlet and outlet temperatures of the circulating water were identical, in which case the temperature of the coil is definitely known, as being the same as that of the water. The heat dissipated from the outer surface of the coil is then the equivalent of the electrical energy wasted in the coil, which is known from measurements of the current supplied. The results of these two series of experiments were in very close agreement, the greatest difference not exceeding 2 per cent., and this difference is, in part, to be accounted for by the slight temperature gradient in the pipe wall when the heat is supplied from the circulating water.

Experiments were carried out in still air, in order to obtain the "radiation" loss, which includes the loss also due to natural convection currents, and at wind speeds up to 2000 cm. per sec. (44·5 miles per hour). In each case the wind speed was measured by a calibrated Pitot tube at a point 6 inches up stream from the forward edge of the coil, and opposite its centre. A preliminary exploration of the area covered by the coil showed that the wind speed was sensibly constant over the whole area. Assuming the heat loss to be proportional to the wind speed V raised to some power n, the value of n was deduced from corresponding pairs of experiments at different wind speeds, but at the same mean temperature.

One aluminium pipe was formed into a grid having 7 parallel legs 18 inches long and 3·2 inch pitch, connected by six U bends. In this case the grid was mounted with its plane perpendicular to the direction of air flow, so as to give the cooling effect due to normal impact of the air current.

The details of the pipes are as follow :—

Material.	Form.	Outside diam. cm.	Thickness. cm.
Aluminium	Coil.	1·124	0·142
Aluminium	Grid.	„	„
Copper	Coil.	1·103	·081
Steel	Coil.	0·925	·056
Steel	Straight pipe.	9·520	·254

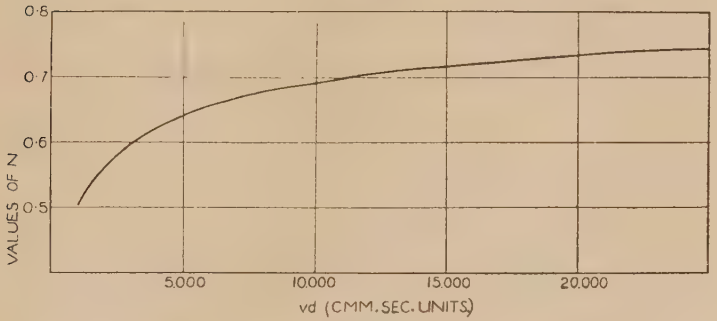
(3) After being tested in the cold drawn state the surfaces of the pipes were treated in various ways, and the pipes were retested. The mean results of a large number of concordant tests are as follow :—

Pipe.	Condition.	Heat loss in calories per sq. cm. per sec. per degree diff. of temp. between water and air at 35° m.p.h. (1568 cm. per sec.)	Heat loss per sq. cm. per degree difference in still air.	Index "n" in $H \propto V^n$.
Aluminium Coil.	Original surface	·00280	·00049	·55
	Sandblasted	·00277	·00053	·55
	Coated with dull black spirit paint	·00293	·00065	·55
	Enamelled black	·00282	·00053	·52
Aluminium Grid.	Original surface	·00330	·00049	·55
Copper Coil	Original surface	·00282	·00053	·50
	Sandblasted	·00284	·00062	·50
	Coated with black spirit paint	·00295	·00065	·50
	Enamelled	·00285	·00056	·50
Steel Coil ...	Original surface	·00327	·00067	·50
	Enamelled black	·00328	·00057	·50
Large Steel Pipe.	Original surface	·00158	.....	·72

In each case the given value of n is the mean over the range of velocities from 800 to 1600 cm. per second. Actually the value of n increases with the velocity and with the diameter of the pipe.

Over a range of velocities from 200 to 2000 cm. per second, its value appears to depend upon the product vd and its approximate values are shown in the curve of fig. 1.

Fig. 1.



(4) *Relative heat dissipation from a pipe coil and from a straight pipe.*—The results of the tests on a pipe coil and on a grid formed of similar pipes mounted normal to the direction of the air flow, show that at speeds between 20 and 45 m.p.h. the heat dissipation is 18 per cent. greater in the latter case.

(5) *Effect of temperature.*—A large number of experiments were carried out to determine the law of variation of heat dissipation with temperature, at a given wind speed. In these the temperature of the hot surface was varied between the limits 30° C. and 90° C., the air temperature being approximately 12° C. Over this range of temperature, the heat loss is proportional, not to the temperature difference θ, but to θ^m, where $m = 1{\cdot}070$ at 800 cm. per sec. and 1·050 at 1600 cm. per sec. This is in general agreement with the results of experiments by Stanton on cylindrical bars * and by Stanton, Booth, and Marshall on copper-finned cylinders †. These results when reduced show $m = 1{\cdot}075$ for an aluminium bar 1·27 cm. diam., 1·065 for a copper bar, at 1100 cm. per sec., and 1·075 for copper fins, over the same temperature range and at about the same mean velocity.

* Advisory Committee for Aeronautics, T. 1010, October 1917.

† Advisory Committee for Aeronautics, T. 929 & I. C. E. 80, April 1917.

(6) *Dimensional effect.*—The principle of dynamical similarity applied to the problem of heat dissipation in an air current, leads to the general result

$$H = \rho l^2 v^3 \phi\left(\frac{\sigma\theta}{v^2}, \frac{k}{\sigma\mu}, \frac{\nu}{lv}\right), \quad . \quad . \quad . \quad . \quad (1)$$

where H is the heat loss per second; ρ the density; σ the specific heat; k the conductivity; μ the viscosity; and ν is the kinematic viscosity.

Since for gases $\frac{k}{\sigma\mu}$ is sensibly constant, this becomes

$$H \propto \rho l^2 v^3 \phi\left(\frac{\sigma\theta}{v^2}, \frac{\nu}{lv}\right), \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which may be written

$$H \propto \rho l^2 v^3 \phi\left(\frac{k\theta}{\rho l v^3}, \frac{\nu}{lv}\right). \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If, as is usually assumed, H is proportional to θ, this becomes

$$H \propto kl\theta\phi\left(\frac{\nu}{lv}\right), \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and if, in addition, H is proportional to v^n,

$$H \propto \frac{kl^{n+1}v^n}{\nu^n} . \theta, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

As applied to one of a series of similar pipes, l in this expression refers to any one definite linear dimension, which may be either the length or diameter of the pipe. If, however, the pipes are long, but not of similar length, since the heat loss is proportional to the length, (5) may be written

$$H \propto \frac{kld^n v^n}{\nu^n} . \theta, \quad . \quad . \quad . \quad . \quad . \quad (5')$$

so that the heat loss per unit length of pipe, per degree difference of temperature, will be

$$\frac{H}{l\theta} \propto k\left(\frac{vd}{\nu}\right)^n,$$

while the heat loss per unit area per degree difference of temperature will, at a given velocity, be proportional to d^{n-1} and, at a given value of vd, will be proportional to $1/d$.

If, however, $H \propto \theta^m$, where m is not unity,

$$H \propto \rho l^2 v^3 \phi\left(\frac{\sigma\theta}{v^2}, \frac{\nu}{lv}\right)$$

$$\propto \rho l^2 v^{3-2m} (\sigma\theta)^m \phi\left(\frac{\nu}{lv}\right). \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If H is also proportional to v^n,

$$\phi\left(\frac{\nu}{lv}\right) = \left(\frac{lv}{\nu}\right)^{n-3+2m}$$

and
$$H \propto \rho l^2 v^n (\sigma\theta)^m \left(\frac{l}{\nu}\right)^{n-3+2m}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

or
$$\frac{H}{l\theta} \propto \frac{\rho v^n \sigma^m \theta^{m-1} d^{n-2+2m}}{\nu^{n-3+2m}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

indicating that, at a given velocity and for given temperatures, the heat loss per unit area should be proportional to d^{n-3+2m} and, per unit length, to d^{n-2+2m}, while for a given value of vd, the loss per unit area should be proportional to d^{2m-3} and, per unit length, to d^{2m-2}.

Since, however, ρ, σ, and ν vary with temperature, and therefore with θ for a given initial air temperature, the variation indicated by the θ^m term will include that due to the changing properties of the air. Neglecting the variation in the specific heat as being negligibly small for the range of temperature usual in cooling problems, it is of interest to note what proportion of the total observed variation is due to the change in ρ and in ν or μ.

Over the range of temperatures from 0 to 100° C., $\mu \propto 1 + \cdot 0026\,T$ approximately *, where T is the temperature in degrees centigrade; while $\rho \propto \frac{1}{T + 273}$. If T° C. is the mean of the temperatures of the inlet air and of the surface it is probably nearly correct to assume that the density and viscosity of the layer of air most directly concerned in the heat dissipation will be that corresponding to this value of T.

The factors ρ and ν are involved in formula (8) in the form $\rho\nu^{3-n-2m}$, or $\rho^{2m+n-2} \cdot \mu^{3-n-2m}$, which is therefore proportional to

$$(T + 273)^{2-n-2m} (1 + \cdot 0026\,T)^{3-n-2m}.$$

In the author's measurements on the two steel pipes of

* Proc. Roy. Soc. A. vol. lxxx. p. 114 (1908).

diameters 0·925 cm. and 9·52 cm. in two experiments (1) and (2), in which the temperature of the surface was respectively 90° C. and 40°, the air temperature was 10° C., so that

$$T_1 = \frac{90+10}{2} = 50° \text{ C.} \quad \text{and} \quad T_2 = 25° \text{ C.}$$

Giving n the mean value for these pipes, viz. 0·61, and taking $m=1·060$, this makes

$$2-n-2m = -·73,$$

and

$$\frac{(T_1+273)^{-·73}(1+·0026\,T_1)^{·27}}{(T_2+273)^{-·73}(1+·0026\,T_2)^{·27}} = \frac{1}{1·045}.$$

The corresponding values of the differences of temperatures between metal and air are 80° and 30°, so that

$$\theta_1/\theta_2 = 2·67 \quad \text{and} \quad (\theta_1/\theta_2)^{1·060} = 2·85 = 1·060\,\theta_1/\theta_2.$$

From this it appears that of the observed 6·0 per cent. increase in the heat loss h per ° C. over this range of temperature, 4·5 per cent. is due to the variation in ρ and μ. Determining by trial the value of m which makes the variation in h proportional to θ^m when the variation in ρ and μ is taken into account, gives $m=1·02$ as compared with the apparent value 1·060 obtained by neglecting this variation.

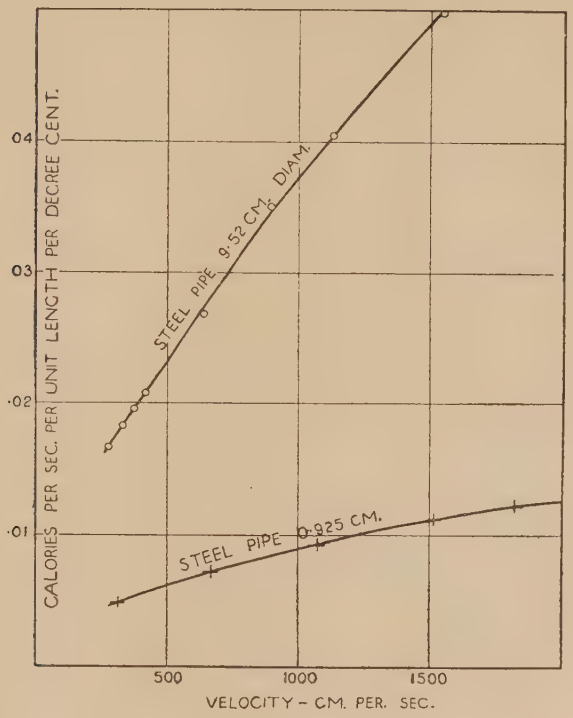
Adopting this value of m in (8), it appears that if the theory of dimensions is to apply to this case of heat transmission the heat loss per unit area per degree at a given velocity and for given temperatures should be proportional to $d^{-·35}$, while for a given value of vd the loss per unit area per degree should be proportional to $d^{-·97}$.

In the two experimental pipes the ratio of the diameters is 10·3. The heat loss per ° C. per cm. length of each pipe is shown in fig. 2. At a velocity of 35 m.p.h. (1568 cm. per sec.) the value of h per sq. cm. per degree is ·00386 for the small pipe and ·00171 for the large one, the ratio being 2·26. The ratio of the two values of $d^{-·35}=2·27$, so that the agreement is almost exact.

Again, at a velocity of 1568 cm. per sec., the value of vd for the small pipe is 1450 cm. sec. For this value of vd, the heat loss per unit area per degree is ·000416 calorie per sec. in the large pipe and ·00386 calorie in the small pipe, the ratio being 9·3. The ratio of the two values of $d^{2m-3}(=d^{-·96})=9·4$, so that here again the agreement is satisfactory.

(7) *Comparison with results by other observers.*—The results of experiments by Hughes on a series of copper cylinders of diameters ·43 cm., ·81 cm., 1·93 cm., and

Fig. 2.



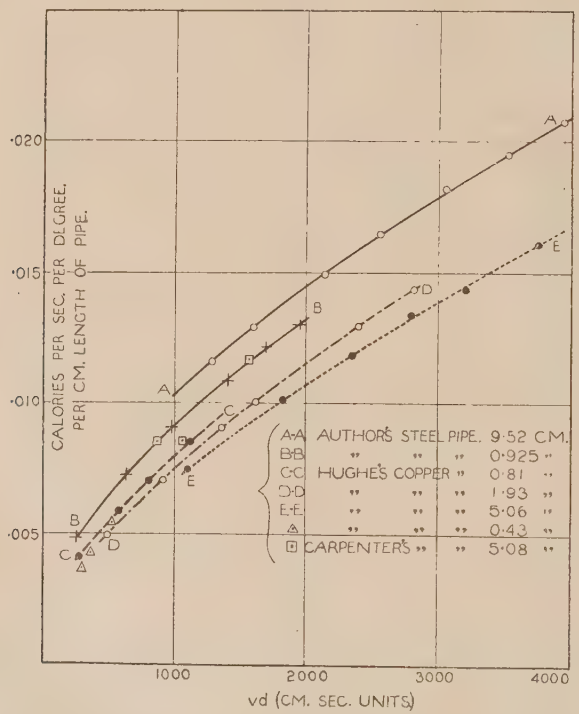
5·06 cm. are indicated by the curves of fig. 3. In these experiments velocities up to 1400 cm. per sec. were used. The copper surface was maintained at a constant temperature of 100° C. throughout and the air temperature was apparently 15° C.* In the original paper the values of the heat loss are given in calories per unit length of the cylinder, and for comparison the results of the present experiments on the large and small steel pipes have been plotted on the same scale.

The results indicate that for a given value of vd the heat

* The air temperature can only be inferred from the original paper. No definite figures are given except in the radiation tests when it was 15° C. It is inferred that it was the same in the convection tests, but to this extent the results are uncertain.

loss per unit length from the author's steel pipes is approximately 20 per cent. greater than the average value obtained by Hughes from the copper pipes having diameters between ·43 cm. and 5·06 cm. Since in the author's tests the steel pipes gave a rate of heat loss 7 per cent. greater than the copper pipes (§ 9), this difference, with pipes of the same material, would be reduced to about 12 per cent. It is, moreover, possible that the velocities of air flow given by

Fig. 3.



Hughes are somewhat too high, since the flow was pulsating and a steady reading of the Pitot gauge could only be obtained by using a very viscous oil. In such a case the velocity as calculated from the mean height of the gauge is too high by an amount which depends on the amplitude and periodicity of the fluctuations, but which might readily amount to as much as 12 per cent.

An examination of Hughes's results shows that for a given value of vd the heat loss per degree per unit length of the pipe in some cases increases and in other cases decreases

with an increase in diameter. Thus a pipe 0·43 cm. diam. has a smaller heat dissipation per unit length than one of 0·81 cm. diam., but the latter has a larger heat dissipation than one either 1·93 cm. or 5·06 cm. diameter. Since all these tests were carried out at the same pipe temperature (100° C.) and presumably at the same air temperature, no data are available as to the variation of the heat loss with θ. If proportional to θ^m where m is greater than unity, the heat loss per unit length for a given vd should increase with the diameter.

The results of the tests on the largest of Hughes's pipes (15·5 cm. diam.) give values of h much greater than those of the author or of the remaining pipes of his own series. Since the lowest value of vd in the tests on this pipe was 5500 the results are not shown on the curves of fig. 3 or fig. 4. For this value of vd the heat loss per unit length per degree is ·034 calorie as compared with ·0257 for the author's pipe 9·52 cm. diam., a difference of 30 per cent. There are, however, reasons for thinking that in this particular pipe, which took the form of a short cylinder only 20 cm. long, and in which the end effects would be relatively large, the results given are too high.

Some results are also available of tests by Carpenter * on a pipe 5·08 cm. diam. These are plotted in fig. 3, and are in fairly close agreement with those of the author.

(8) A more testing confirmation of the validity of the dimensional theory is afforded by a comparison with the results obtained by King † on small platinum wires from ·003 to ·015 cm. diam. at velocities between 17 and 900 cm. per sec. As a result of these experiments, he gives a formula which may be written

$$h/\theta = \mathrm{B}\sqrt{vd}\,\sigma\mathrm{C},$$

where h is the heat loss per cm. length of wire and B and C are sensibly constant. As pointed out by Davis this corresponds to a value of $h=0{\cdot}66$ calorie per unit length when $vd=1000$ if the temperature of the wire is 100° C. and if that of the air is 15° C. This makes the heat loss per unit length per degree equal to ·00776 calorie per sec. Comparing the largest of the author's pipes (9·52 cm.) with the smallest of King's wires (·003 cm.), the ratio of diameters is 3170, and the ratio of the values of $d^{2m-2}=d^{\cdot 04}=1{\cdot}38$.

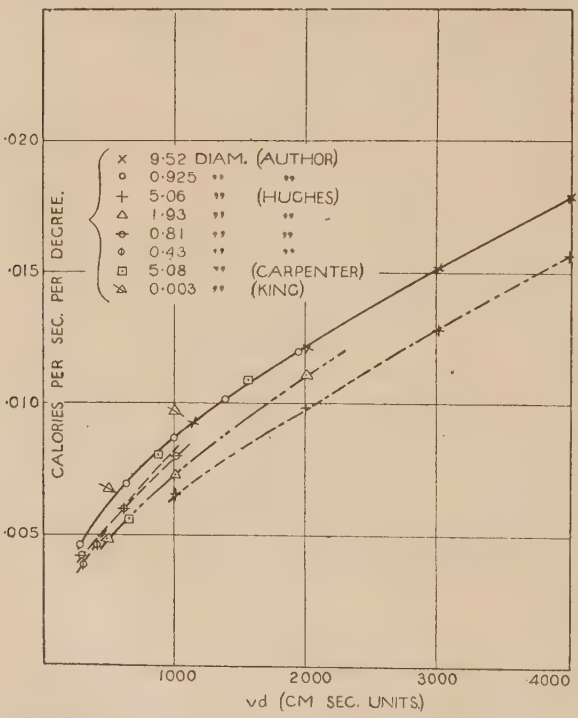
* Quoted by Langmuir, Trans. Am. Electro-Chem. Soc. xxiii. p. 324 (1913).

† Phil. Trans. ccxiv. p. 373 (1914).

According to the dimensional theory the heat loss per unit length from the large pipe when $vd=1000$ should therefore be $\cdot00776 \times 1\cdot38 = \cdot0107$ calorie per sec. per degree. The value computed from the author's experiments is ·0104, so that over this very large ratio of diameters the agreement is extremely close.

In fig. 4 curves are plotted to represent the heat loss per

Fig. 4.—Heat loss per unit length of a pipe 1 cm. diam. as deduced from tests on pipes and wires having diams. ranging from ·003 cm. to 9·52 cm.



unit length of a 1 cm. pipe per °C. as deduced from the mean results of the tests on each of the above mentioned pipes on the assumption that the heat loss per unit length is proportional to $d^{\cdot04}$. The author's values for the steel pipes have been reduced by 7 per cent. so as to represent the values for copper pipes.

The results deduced from the experiments of King, Carpenter, and the author agree very closely, while those of the smaller pipes of Hughes are in fair agreement, but are lower.

(9) *Effect of material and roughness of surface on rate of heat dissipation.*—Since the small pipes used in the author's coil experiments are not of identical diameters, the values of the heat loss given in Table I. for the different surfaces are not directly comparable. Correcting these, however, for the small differences in diameter, according to the relationship

$$\frac{H}{ld\theta} \propto d^{n-3+2m},$$

where $m=1{\cdot}02$, so as to give the loss per unit area of a series of pipes of the same diameter (0·925 cm.) as the steel coil, the following results are obtained :—

TABLE II.

Pipe.	Surface.	Heat loss in calories per sq. cm. per sec. per ° C. difference of temperature between water and air at 35 m.p.h.
Aluminium	Original surface	·00305
	Sandblasted	·00302
	Coated with dull black spirit paint	·00319
	Enamelled black	·00309
Copper	Original surface	·00304
	Sandblasted	·00306
	Coated with black paint	·00318
	Enamelled black	·00307
Steel	Original surface	·00327
	Enamelled black	·00328

From these it appears that the original surface of the steel pipe gives a slightly greater (about 7 per cent.) heat dissipation than that of the aluminium or copper pipes, which are identical. This is apparently due to the fact that the steel pipe was not bright, but had a dull dark finish resulting in a greater loss by radiation than in the other pipes, which were bright though not polished. The effect of the roughening of the surface produced by sandblasting is negligibly small. A coating of black enamel increases the heat transmission of a copper or aluminium pipe by about 1 per cent., but this effect is in all probability due to the fact that the effective diameter is increased by this coating. A coating of dull black spirit paint on a copper or aluminium pipe

increases the heat dissipation by 4·5 per cent. at this air speed, this effect being largely due to the fact that it increases the radiation loss.

(10) *Conclusions.*—The results of the investigation indicate :—

(*a*) At normal air temperatures, and with a hot cylindrical surface at temperatures between 40° C. and 100° C., the heat loss in a cooling wind is proportional to θ^m, where θ is the difference of temperature and m has a value of 1·02.

(*b*) If the changes in density and viscosity of the air with a change in temperature are neglected, the effective value of m is approximately 1·06.

(*c*) Taking account of the changes in viscosity and density, the theory of dimensional similarity holds with reasonable accuracy over a range of diameters from ·003 cm. to 10·0 cm. and for velocities up to 1500 cm. per sec.

(*d*) The value of the index n in $H \propto v^n$ varies with v and with d. For a given value of vd it is approximately constant. It increases from ·50 with small pipes at low velocities up to ·72 with large pipes at velocities in the neighbourhood of 1800 cm. per sec.

(*e*) Except for the greater radiation loss with pipes of dull, dark surfaces, the kind of surface has little effect on the heat loss. The degree of roughening produced by sandblasting has no appreciable effect.

(*f*) For copper cooling pipes, the heat loss "h" in calories per cm. of length per degree difference of temperature is given by $h = Kd^{\cdot 04}$, where K may be taken as having the following values :—

vd (cm. sec. units).	500	1000	2000	3000	4000	5000	10,000	15,000
h	·0062	·0087	·0122	·0152	·0180	·0207	·0320	·0425

For steel pipes, or for pipes painted black, the value of K is to be increased by 5 per cent.

These values apply to wires and to long pipes or cylinders having diameters up to 10 cm. with normal air impact. If formed into a coil with the axis of the coil perpendicular to the direction of air flow, they are to be reduced by 18 per cent.

XXIX. *Recombination of Gaseous Ions, the Chemical Combination of Gases, and Monomolecular Reactions.* *By* Sir J. J. Thomson, *O.M., F.R.S., Master of Trinity College, Cambridge* *.

IF two ions, one at A and the other at B, are left to themselves, they will ultimately separate to an infinite distance if

$$\frac{1}{2}\frac{M_1M_2}{M_1+M_2}(V_1^2+V_2^2-2V_1V_2\cos\theta) > \frac{\mu}{AB}. \quad . \quad (1)$$

M_1, M_2 are the masses of A and B respectively, V_1, V_2 their velocities, θ the angle between V_1 and V_2, μ/r^2 the attraction between A and B when separated by a distance r.

Gaseous ions possess in virtue of thermal agitation a finite amount of energy. We shall suppose that each ion has the mean kinetic energy corresponding to its absolute temperature. If this temperature is θ, then

$$\tfrac{1}{2}M_1V_1^2=\tfrac{1}{2}M_2V_2^2=\tfrac{3}{2}R\theta=\beta\theta, \quad \text{where } \beta=2{\cdot}02\times10^{-16}.$$

Substituting these values in (1) and assuming that $\cos\theta$ has its mean value zero, we find that the ions will separate to an infinite distance unless

$$\beta\theta < \frac{\mu}{AB}.$$

Hence, if the ions at A and B possess kinetic energy corresponding to the temperature, they will not recombine if they are at a greater distance apart than $\mu/\beta\theta$. This is on the assumption that they are not subject to any influence other than their mutual attraction. If they are moving through a gas, they may lose some of the kinetic energy which would enable them to separate by one or other of them when they are close together coming into collision with a molecule of the gas.

On the assumption that collision with a molecule restores the kinetic energy of the ion to $\beta\theta$, its value for thermal equilibrium, we see from the preceding investigation that to be effective in preventing separation the collision must occur when the distance between A and B is less than $\mu/\beta\theta$, and that every such collision is effective in producing recombination between A and B.

Hence, to find the number of recombinations per second between the A and B ions, we must describe round the

* Communicated by the Author.

A particles spheres with radii $\mu/\beta\theta$, and find the number of collisions made by the B particles in one second with the molecules of the gas inside these spheres; then describe another set of spheres with the same radius round the B particles, and find the number of collisions per second made by the A particles with the molecules of gas inside these spheres; the sum of the numbers of these two sets of collisions will be the number of recombinations of the A and B ions per second.

If all directions of motion of the A and B particles are equally probable, the number of B particles passing through a sphere round an A particle per second is

$$\pi d^2 \rho' \{U_A^2 + U_B^2\}^{1/2},$$

where $d = \mu/\beta\theta$, ρ' is the number of B particles per unit volume, U_A and U_B the average velocities of the A and B particles respectively.

The number of A particles passing through a sphere round a B particle is

$$\pi d^2 \rho \{U_A^2 + U_B^2\}^{1/2},$$

where ρ is the number of A particles per cubic centimetre.

We proceed to calculate the number of collisions made by the ions in passing through these spheres.

The chance that a B ion will pass through a distance x without making a collision is $\epsilon^{-\frac{x}{\lambda'}}$, where λ' is the mean free path of the ion. If the direction of motion of the ion when it enters the sphere makes an angle ψ with the normal, the length of the undisturbed path in the sphere is $2d\cos\psi$. The chance of the angle ψ being between ψ and $\psi + \delta\psi$ is $\sin\psi\, d\psi$. Hence the chance of the ion getting through the sphere without making a collision is

$$\int_0^{\frac{\pi}{2}} \epsilon^{-\frac{2d\cos\psi}{\lambda'}} \cdot \sin\psi\, d\psi = \frac{\lambda'}{2d}\left(1 - \epsilon^{-\frac{2d}{\lambda'}}\right).$$

The chance that it makes a collision is therefore

$$1 - \frac{\lambda'}{2d}\left(1 - \epsilon^{-\frac{2d}{\lambda'}}\right).$$

The chance is, in fact, somewhat greater than this, since the actual path is longer than the undisturbed one.

If, as we have supposed, each collision inside the sphere

results in the combination of the ions, the number of recombinations per second due to the B ions making collisions with the molecules of the gas is

$$\pi d^2 \rho\rho' (U_A^2 + U_B^2)^{1/2} \left(1 - \frac{\lambda'}{2d}\left(1 - \epsilon^{-\frac{2d}{\lambda'}}\right)\right).$$

Similarly, the number of recombinations due to the A ions coming into collision with the molecules of the gas is

$$\pi d^2 \rho\rho' (U_A^2 + U_B^2)^{1/2} \left(1 - \frac{\lambda}{2d}\left(1 - \epsilon^{-\frac{2d}{\lambda}}\right)\right),$$

where λ is the mean free path of an A ion through the gas.

Hence, taking both the A and B collisions into account, we see that the number of recombinations per unit volume per second is equal to

$$\pi d^2 \rho\rho' \{U_A^2 + U_B^2\}^{1/2} \left(1 - \frac{\lambda}{2d}\left(1 - \epsilon^{-\frac{2d}{\lambda}}\right) + 1 - \frac{\lambda'}{2d}\left(1 - \epsilon^{-\frac{2d}{\lambda'}}\right)\right).$$

But this number is by definition equal to $\alpha\rho\rho'$ if α is the coefficient of recombination of the ions; hence

$$\alpha = \pi d^2 (U_A^2 + U_B^2)^{1/2} \left(1 - \frac{\lambda}{2d}\left(1 - \epsilon^{-\frac{2d}{\lambda}}\right) + 1 - \frac{\lambda'}{2d}\left(1 - \epsilon^{-\frac{2d}{\lambda'}}\right)\right). \quad . \quad . \quad . \quad (2)$$

Since the attraction between the ions is due to their electrical charges $\mu = e^2$, where e is the charge on an electron, d is given by the equation

$$\frac{e^2}{d} = \beta\theta, \quad \text{where } \beta = 2{\cdot}02 \times 10^{-16}$$

at 0° C., $\theta = 273$ and $\beta\theta = 5{\cdot}5 \times 10^{-14}$ erg, and since

$$e = 4{\cdot}8 \times 10^{-10}, \quad d \text{ at } 0^\circ \text{ C.} = 4{\cdot}18 \times 10^{-6} \text{ cm.}$$

The value of d varies inversely as the absolute temperature, but is independent of the pressure of the gas; at 0° C. d is large compared with atomic dimensions, and is comparable with the mean free path of an air molecule at atmospheric pressure.

The value of λ, for an oxygen molecule through oxygen at 0° C. and atmospheric pressure, is $1{\cdot}02 \times 10^{-5}$ cm., which is about 2·5 times the value of d; so when the pressure is reduced much below 760 mm., d/λ will be a small quantity.

When d/λ is small,

$$1-\frac{\lambda}{2d}\left(1-\epsilon^{-\frac{2d}{\lambda}}\right)=\frac{d}{\lambda};$$

so that in this case we get by equation (2)

$$\alpha = 2\pi(U_A^2+U_B^2)^{1/2}d^3\left(\frac{1}{\lambda}+\frac{1}{\lambda'}\right). \quad . \quad . \quad . \quad (3)$$

When $2d/\lambda$ is large,

$$1-\frac{\lambda}{2d}\left(1-\epsilon^{-\frac{2d}{\lambda}}\right)=1$$

and

$$\alpha = 2\pi(U_A^2+U_B^2)^{1/2}d^2. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Variation of α with the Pressure.

Since λ and λ' are inversely proportional to the pressure, while d, U_A, and U_B do not alter with it, it follows from equation (3) that at low pressures α is directly proportional to the pressure; while at high pressures, when $2d/\lambda$ is large, equation (4) shows that α is independent of the pressure. Thirkill, who has made measurements of α for several gases through a wide range of pressures (Proc. Roy. Soc. lxxxviii. p. 490), finds that unless the pressure exceeds a certain value, which is a considerable fraction of an atmosphere, α is directly proportional to the pressure; while the experiments of Langevin and McClung show that at pressures higher than one atmosphere the rapid increase of α with the pressure does not continue; α seems to attain a maximum value at a pressure of several atmospheres, and then decreases as the pressure increases. Equation (2) indicates that α would approach asymptotically a constant value as the pressure increases, but would not attain a maximum and then decline.

Numerical Values of α.

If we suppose that the ions in air are charged molecules, and that the average velocity and free path are the same as for an uncharged molecule of oxygen, then at 0° C. and 760 mm.

$$U_B = U_A = 4{\cdot}25\times10^4 \text{ cm./sec.},$$
$$\lambda = \lambda' = 1{\cdot}02\times10^{-5} \text{ cm.}$$

Substituting these values in equation (2), we find

$$\alpha = 1{\cdot}96\times10^{-6} \text{ at } 0^\circ \text{ C. and } 760 \text{ mm.},$$

while the limiting value at very high pressures would be

$$\alpha = 6{\cdot}5\times10^{-6}.$$

The value found for α for air at 0° C. and 760 mm. by Thirkill (Proc. Roy. Soc. lxxxviii. p. 490) is $1{\cdot}728 \times 10^{-6}$; so that the agreement is quite close. It is closer, indeed, than we should expect, for the free path which we have used in calculating the numerical value of α is that of an uncharged molecule, while the value of λ which occurs in the theoretical value of α is determined by the distance the ion travels through the gas before losing an appreciable amount of energy. The range of action of a charged molecule will be greater than that of an uncharged one: it will therefore be able to communicate its energy to a greater number of molecules; so that the length of path which a charged particle has to travel to lose a definite portion of its energy is shorter than that which would have to be travelled by an uncharged one. This would make the value of λ we have taken too large: on the other hand, if the ions are aggregates of two or more molecules and not single molecules, the values we have taken for U_A will also be too large; so that the two effects will compensate each other to some extent. We shall return to this point as soon as we have considered the effect of temperature on the value of α.

Variation of α with Temperature.

Of the quantities occurring in the expression for α, d is inversely proportional to the absolute temperature θ, while U_A and U_B are proportional to $\theta^{1/2}$; hence we see from (3) and (4) that at low pressures α is proportional to $\theta^{-3}\theta^{1/2}$ or $\theta^{-5/2}$, while at high pressures it is proportional to $\theta^{-2}\theta^{1,2}$ or $\theta^{3,2}$. In addition to this, there may be, as we shall see, a variation of λ with θ.

The variation of α with temperature has been measured by Erikson (Phil. Mag. xviii. p. 328, 1909, and xxiii. p. 747, 1912), whose experiments were made at constant density, and by Phillips (Proc. Roy. Soc. A, lxxxiii. p. 246, 1910), who worked with constant pressures. Both found a rapid diminution in α as the temperature increased. The relative values of α found by Eriksen for hydrogen at different temperatures are as follows:—

Temp. Abs.	α.
94	6·00
209	·900
296	·45

The Effect of a Charge of Electricity on the Free Path of a Particle.

If M_1, M_2 are the masses of two colliding particles, the transfer of kinetic energy from one to the other produced by a collision is equal to

$$\frac{4M_1M_2}{(M_1+M_2)^2}T\sin^2\theta,$$

where 2θ is the angle through which the relative velocity of the particles is turned by the collision, 2T is the product of the momentum of the system, the relative velocity of the particles, and the cosine of the angle between these vectors. If either of the particles is at rest, T is thus the kinetic energy of the other; if the masses are equal, T is the difference between the kinetic energies of the two particles.

If one of the particles carries an electric charge and the other is an uncharged molecule, the deflexion 2θ will be due to the attraction exerted by the charge on the molecule. This will be similar in character to that between an electric charge and an uncharged metal sphere, which varies inversely as the fifth power of the distance between the charge and the sphere, provided this distance is considerable in comparison with the radius of the sphere. We shall proceed to calculate the value of θ on the supposition that the law of force between the charged ion and the uncharged molecule is expressed by Ku^5 where $u=1/AB$, AB being the distance between the ion and the molecule. With this law of force the equation of the orbit of the molecule relative to the ion is

$$\frac{d^2u}{d\theta^2}+u=\frac{Ku^3}{h^2},$$

where

$$h^2=V^2p^2\frac{M_1M_2}{M_1+M_2},$$

where V is the initial velocity of B relative to A, and p the perpendicular from A on V.

Integrating this equation, we have

$$h^2\left(\left(\frac{du}{d\theta}\right)^2+u^2\right)=\frac{Ku^4}{2}+MV^2,$$

where M is written for $M_1M_2/(M_1+M_2)$,

$$\left(\frac{du}{d\theta}\right)^2=\frac{Ku^4}{2h^2}-u^2+\frac{MV^2}{h^2}. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The apsidal distances are given by equating the right-hand side of this expression to zero; they are the roots of the equation

$$u^4 - \frac{2MV^2p^2}{K}u^2 + \frac{2MV^2}{K} = 0; \quad . \quad . \quad . \quad . \quad (6)$$

for these roots to be real

$$p^4 > 2K/MV^2.$$

For values of p less than this there will be no apsidal distances; the bodies will come together and collide. If the collisions are like direct collisions between elastic spheres, the relative velocity will be reversed by the collision and the bodies will retrace their paths. In this case the relative velocity would be unaltered in magnitude and reversed in direction by the collision, so that θ will be $\pi/2$ and $\sin\theta$ unity.

If b be the value of u at an apse, then by (5)

$$\left(\frac{du}{d\theta}\right)^2 = \frac{K}{2MV^2p^2}(b^2-u^2)\left(\frac{2MV^2}{Kb^2}-u^2\right).$$

So that if $u=b\sin\psi$, we have

$$d\theta = \left(\frac{2MV^2p^2}{K}\right)^{1/2} \frac{d\psi}{\left(\frac{2MV^2}{Kb^2} - b^2\sin^2\psi\right)^{1/2}}.$$

If $k^2 = \frac{Kb^4}{2MV^2}$, this may be written

$$d\theta = (1+k^2)^{1/2} \frac{d\psi}{(1-k^2\sin^2\psi)^{1/2}}.$$

The angle 2θ through which the relative velocity of the two particles is twisted is by fig. 1 equal to

$$\pi - 2\int_0^b \frac{d\theta}{du}\,.\,du$$

$$= \pi - 2\int_0^{\frac{\pi}{2}} (1+k^2)^{1/2} \frac{d\psi}{(1-k^2\sin^2\psi)^{1/2}}$$

$$= \pi - 2(1+k^2)^{1/2}\,\mathrm{F}(k),$$

where

$$\mathrm{F}(k) = \int_0^{\frac{\pi}{2}} \frac{d\psi}{(1-k^2\sin^2\psi)^{1/2}}.$$

Hence

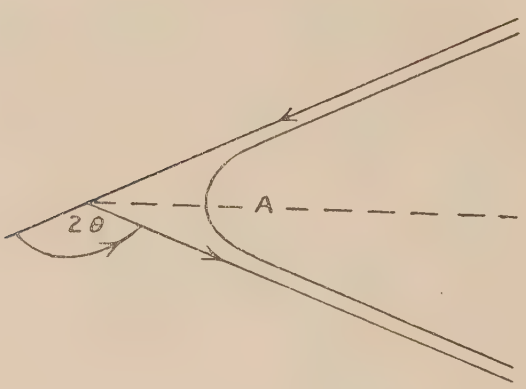
$$\sin\theta = \sin\left(\frac{\pi}{2} - (1+k^2)^{1/2}\,\mathrm{F}(k)\right)$$

$$= \cos\,(1+k^2)^{1/2}\,\mathrm{F}(k).$$

Thus

$$\frac{4\mathrm{M}_1\mathrm{M}_2}{(\mathrm{M}_1+\mathrm{M}_2)^2}\,\mathrm{T}\sin^2\theta = \frac{4\mathrm{M}_1\mathrm{M}_2}{(\mathrm{M}_1+\mathrm{M}_2)^2}\,\mathrm{T}\cos^2\left((1+k^2)^{1/2}\,\mathrm{F}(k)\right).$$

Fig. 1.



If there are N molecules per cubic centimetre in the gas through which the ion is moving, there will be $\mathrm{N}2\pi p\,\delta p$ collisions per unit length of its path for which p is between p and $p+\delta p$. Hence the loss of energy per cm. due to the collisions between the ion and the molecules is

$$\frac{4\mathrm{M}_1\mathrm{M}_2}{(\mathrm{M}_1+\mathrm{M}_2)^2}\,\mathrm{T}\int\cos^2\left\{(1+k^2)^{1/2}\,\mathrm{F}(k)\right\}\mathrm{N}2\pi p\,.\,dp.$$

The lower limit for p, as we have seen, is given by

$$p^4 = 2\mathrm{K}/\mathrm{MV}^2,$$

and the upper limit is infinity.

Since

$$p^2 = \frac{k^2+1}{k}\sqrt{\frac{\mathrm{K}}{2\mathrm{MV}^2}},$$

$$2\pi p\,\delta p = \pi\left(1-\frac{1}{k^2}\right)\sqrt{\frac{\mathrm{K}}{2\mathrm{MV}^2}}\,.\,\delta k,$$

and the limits of k corresponding to those we have prescribed for p are 0 and 1, hence the loss of energy per cm. of path of the ions is

$$\frac{4M_1M_2}{(M_1+M_2)^2}TN\pi\left\{\frac{K}{2MV^2}\right\}^{1/2}\int_0^1\left(1-\frac{1}{k^2}\right)\cos^2\left((1+k^2)^{1/2}F(k)\right)dk.$$

The definite integral is a numerical constant which, using Legendre's Tables for $F(k)$, I find by quadratures to be about ·20. From $p=0$ to $p^2=(2K/MV^2)^{1/2}\sin^2\theta=1$ and the loss of energy per cm. from these collisions is therefore

$$\frac{4M_1M_2}{(M_1+M_2)^2}T\,.\,N\pi\left(\frac{2K}{MV^2}\right)^{1/2}.$$

Thus the total loss of energy due to the collisions is, per unit length of path of the ion,

$$\frac{4M_1M_2}{(M_1+M_2)^2}T\,.\,N\pi\,.\,1{\cdot}1\left(\frac{2K}{MV^2}\right)^{1/2}.$$

This loss of energy is due to the charge on the ion; but even if the ion had not been charged, it would have made collisions which would have produced a transfer of energy. If we suppose that these collisions are like those between elastic spheres; then if s is the sum of the radii of two spheres and p the perpendicular from the centre of one on the velocity of the second sphere relative to the first, then

$$\sin^2\theta=1-\frac{p^2}{s^2}$$

and

$$\int_0^\sigma\sin^2\theta\,N2\pi p\,dp=\tfrac{1}{2}N\pi s^2.$$

When we are dealing with the problems on the transference of energy, we may regard $2N\pi s^2M_1M_2/(M_1+M_2)^2$ as the measure of the reciprocal of the energy free-path of the uncharged molecule, for it measures the number of times per unit length of path that the maximum transfer of energy takes place. When the molecule is charged, the reciprocal of its free path will for the same reason be measured by

$$4M_1M_2N\pi\times1{\cdot}1(2K/MV^2)^{1/2}/(M_1+M_2)^2$$

Hence, if λ is the energy free-path when the molecule is uncharged, λ' that when it is charged,

$$\lambda'=\frac{\lambda}{2{\cdot}2(2K/s^4MV^2)^{1/2}}.$$

Hence, if the free path of the charged molecule is to be much less than that of the uncharged one, $K/2s^4MV^2$ must be considerable.

This quantity is the ratio of $K/4s^4$, the work required to separate an uncharged from a charged molecule with which it is in contact, to $MV^2/2$, the energy possessed by a molecule in virtue of its thermal agitation. We have assumed that there were no collisions for the apsidal orbits, hence $s^4 < 2K/MV^2$ or $2K/s^4MV^2 > 1$).

This result is interesting in connexion with the explanations which have been advanced to account for the smallness of the mobility of the gaseous ions under electrical forces. One theory is that the ions are not simple molecules, but aggregates of a charged molecule with other molecules; another theory is that the small mobility is due to the diminution in the length of the free path caused by the electrical charge on the ion. We shall see, however, later on that the condition that a charged molecule should form aggregates with the other molecules is that K/s^4MV^2 should be considerably greater than unity; but this, as we have just seen, is the condition that there should be a large diminution in the free path of the ion owing to its charge.

Thus the two theories are not alternatives, but inseparable. If complex molecules are formed, there must be an appreciable effect on the free path, and if there is a large effect on the free path, complex molecules must be formed.

We have seen that, when the force between the moving particle and the surrounding molecules varies inversely as the fifth power of the distance, the free path is of the form

$$\lambda' = \frac{\lambda}{1 + \alpha(w/\theta)^{1,2}},$$

where w is the work required to separate the moving particle from contact with a molecule, and θ is the absolute temperature.

If the force between the moving particle and the molecules varied inversely as the third power of the distance, we can show by the same method that the free path would be of the form

$$\lambda' = \frac{\lambda}{1 + \beta w/\theta}.$$

The higher the inverse power of the distance which expresses the law of force between the moving particle and the molecules, the lower will be the power to which (w/θ) occurs in the expression for the modified free path. Since one uncharged molecule exerts forces on another, it follows

from the preceding investigation that the free path in a gas in a normal state must be a function of w/θ, where w is the work required to split up an aggregate of two molecules. The conclusion that the free path of a molecule depended upon the temperature was put forward many years ago by Sutherland, and determinations of the constant C on the assumption that $\lambda \propto 1/(1+C/\theta)$ have been made by several observers. These values are given in Jeans's 'Dynamical Theory of Gases,' p. 304. Thus for CO_2, C was shown by Sutherland to be 277. Thus at 0° C., C/θ would be approximately unity. We may take this as indicating that the work required to separate two molecules of CO_2 is neither a very large multiple nor a small fraction of the energy of thermal agitation at 0° C.; this corresponds to about 1/30 of a volt.

The value of C for hydrogen is only about 72—about one-quarter of that for CO_2; hence we should expect the work required to separate two hydrogen molecules would be about one-quarter of that required to separate two molecules of CO_2.

Free Path of an Electron.

The case when the moving particle is an electron requires special consideration, since the mass of an electron is exceedingly small compared with that of the molecules with which it collides. We see from the expression on p. 342 that when two colliding bodies have very different masses, the transference of energy by a collision is very small; so that between an electron and a mass as great as that of a molecule there will be very little transference of energy at a collision. Thus, if the gas through which the electrons were moving were hydrogen, the energy transferred at a collision between an electron and a molecule would be only 2/1800 of that transferred if instead of an electron a hydrogen molecule were moving with the same energy.

It follows from this that the main loss of energy by the electrons is not by collision with the molecules as a whole, but with the individual electrons in the molecule. These electrons have definite periods of vibration, and the amount of energy transferred to them by collision with an electron moving with a definite speed will vary very greatly with the frequency of these vibrations.

The energy the moving electron gives up at a collision with an electron oscillating about a fixed position depends upon the relation between the time of vibration of the fixed electron and the time taken by the moving electron to pass

over a space equal to the minimum distance between the two electrons. The force between the electrons varies as $1/r^2$; and if c is the minimum distance, v the velocity of the moving electron when in this position, and t the time reckoned from the instant when it passes through the apsidal distance, $r^2 = c^2 + v^2t^2$ with considerable accuracy. The equation of motion of the fixed electron is

$$m\left(\frac{d^2x}{dt^2} + n^2x\right) = \frac{e^2}{c^2 + v^2t^2},$$

where n is the frequency of the oscillation. The amplitude of the displacement x produced by the collision will be

$$\frac{e^2}{mn}\int \frac{\cos nt}{c^2 + v^2t^2} dt.$$

We may, since the force only produces a measurable effect when the electrons are near together, take $-\infty$ and $+\infty$ as the limits of integration, since

$$\int_{-\infty}^{+\infty} \frac{\cos nt}{c^2 + v^2t^2} dt = \frac{\pi}{cv} \epsilon^{-\frac{nc}{v}},$$

the displacement produced by the collision is

$$\frac{e^2\pi}{mn\,cv} \epsilon^{-\frac{nc}{v}},$$

and the energy given to the vibrating electron is

$$\frac{1}{2} \frac{e^4\pi^2}{m\,c^2v^2} \epsilon^{-\frac{2nc}{v}}.$$

This expression vanishes when $v = 0$, and when $v = \infty$, it has a maximum value for $v = nc$, and is very small for values of v which are either very small or very large in comparison with this critical value.

If T is the time of vibration of the electron, $T = 2\pi/n$; so that the critical velocity, *i. e.* the velocity at the apsidal distance for maximum transference of energy, is given by the equation

$$v\mathrm{T} = 2\pi c.$$

An electron moving with this velocity would pass over the orbit $2\pi c$ in the time of vibration of the electron which receives the energy. As the apsidal distance c is of the order of the distance of an electron from the central positive charge, the orbit $2\pi c$ would be comparable with an orbit of an electron within the atom, and if an electron describes this orbit in the

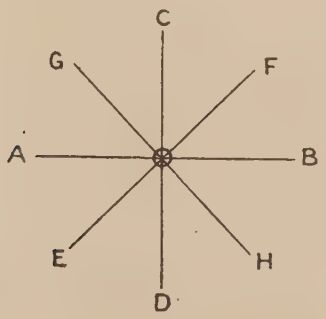
time of vibration of one of the electrons, its energy must be comparable with that required to eject the electron from the molecule—*i. e.*, the maximum transference of energy takes place when the energy of the moving electron is of the same order as the ionizing potential.

Until the critical velocity is reached, the transference of energy increases with the energy of the moving electron; after passing the critical velocity the transference decreases as the velocity of the moving electron increases, and the decrease goes on until the energy of the moving electron approaches that corresponding to another ionizing potential greater than the first, when the transference of energy increases to another maximum and then diminishes again.

The velocity v which occurs in the expression for the transference of energy is the velocity at the apsidal distance, and not V the velocity before the collision occurs. The connexion between V and v will depend upon the distribution of positive charges and electrons in the molecule which contains the vibrating electron, for these, as well as the electron with which it collides, affect the motion of the moving electron before the collision takes place.

Thus suppose the molecule with which the electron collides consists of two positive charges A and B and two electrons

Fig. 2.



C and D at the corners of a square. Then, if the moving electron attains its apsidal distance from C within the regions GOF, EOH, where GH and EF bisect the sides of the square at right angles, the velocity v will be less than the velocity of projection; if it attains the apsidal distance within GOE or HOF, the velocity v will be greater than V; and if the electron is at its apsidal distance from C when near A or B, v may be very much greater than V.

We saw from the expression for the transference of energy that but little energy is transferred when $2nc/v$ is large. The forces outside a neutral molecule are very small at distances considerably greater than the radius of the molecule, so that c will be of the order of the radius of a molecule. If V has the value corresponding to thermal agitation at 0° C., $V = 10^7$, and if $c = 10^{-8}$, then

$$\frac{4\pi c}{T V} = \frac{4\pi \times 10^{-15}}{T}.$$

A value of T equal to $4\pi \times 10^{-15}$ would correspond to a wave-length of about 38,000 Ångström units; as the vibrations of electrons have a much shorter wave-length than this, T must be very much less than $4\pi \times 10^{-15}$; so that, unless the electron gets very much accelerated before the collision, very little energy will be transferred at a collision. Herz found, however, that electrons with this initial velocity lost when passing through hydrogen a few per cent. of their energy at each collision; this is far greater than the energy which would be transferred by a collision between the electron and the molecule if the electrons in the molecule were not thrown in vibration, for this would only be 4 × mass of electron / (mass of hydrogen molecule) or 1/900, and also far more than would be transferred by setting the electron in vibration unless the moving electron was greatly accelerated before the collision.

If the electron was so projected that the apse occurred near to either A or B (fig. 2), it would, through the action of the stray field of the molecule, acquire an amount of energy comparable with the ionizing potential, and would therefore lose a considerable amount of energy by the collision. If the initial energy is small compared with the ionizing potential, only a very small fraction of the collisions will result in the apse occurring near A or B; in the other collisions there will be too small an increase of energy to give rise to an appreciable transfer. Thus the average loss at a collision will be but small, but would be sufficient to account for the losses observed by Herz.

When the initial value of the velocity is not far from the critical value, the greatest transference of energy will take place when the apse is in a part of the molecule where the potential differs from that at an infinite distance by a small fraction of the ionizing potential; as this region occupies the greater part of the molecule, a very large fraction of the collisions will result in a transference of the greater part of the energy of the moving molecule to the vibrating one. In this

case the energy free-path of the moving electron will be nearly the same as the geometrical free-path; with smaller velocities the energy free-path will be much longer than the geometrical one.

Rate of Recombination of Electrons and Positive Ions.

In the calculation of the rate of recombination of positive and negative ions given on p. 339, we have assumed that the collision of either a positive or a negative ion with a molecule results in an appreciable loss of kinetic energy by the pair of ions. This will be the case when the masses of the positive and negative ions are not very unequal, for then the increase in the kinetic energy of the pair due to their approach under their attraction will be shared between the ions, so that the energy of each will be increased by a finite amount, which it will lose by collision. When, however, the masses are as different as they are when the carrier of the negative charge is an electron and of the positive charge a positive ion, the increase in the kinetic energy when they approach is practically confined to the body of small mass—the electron,—so that the positive ion has none to lose on collision. In this case the only collisions that give rise to a loss of energy are those of the electrons, and at low pressures the expression for the rate of recombination will be

$$\pi d^3\{U_+^2+U_-^2\}^{1.2}\frac{1}{\lambda_-},$$

where λ_- is the mean free path of an electron, and U_+ and U_- the mean velocities of the positive ion and electron respectively. As U_- is large compared with U_+, the rate of recombination of an electron and a positive ion is approximately $\pi d^3 U_-/\lambda_-$. Since d is the same as for two ions, the rates of recombination for electron and positive ion and for negative and positive ions are as U_-/λ_- is to $2\sqrt{2}U_+/\lambda_+$, assuming that the U's and λ's for the negative ion are the same as for the positive.

The velocity and free path are both greater for the electron than for the positive ion; the value of the ratio of U/λ may depend upon the nature of the gas. Thus for hydrogen, if the positive ion is the molecule, and the electron is in thermal equilibrium with the molecules, the average velocity of the electron is about 60 times that of the molecule. If we take the loss of energy of an electron at a collision as 6 per cent. (see Herz, *Deuts. Phys. Gesell. Verh.* xix. p. 268), it will take some 16 collisions to transfer the energy from the

electron to the molecules, so that the energy free-path will be about 16 times the geometrical one ; but the geometrical free-path of the electron is 2·8 times that of a hydrogen molecule, so that the energy free-path of an electron is 44·8 times that of a hydrogen molecule, hence when the free path of the positive ion is the same as that of the molecule

$$U_- = 60\, U_+,$$

$$\lambda_- = 44{\cdot}8\, \lambda_+.$$

So that $U_-/\lambda_- = 1{\cdot}3\, U_+/\lambda_+$, and the rate of recombination of electrons and positive ions would be $1{\cdot}3/2\sqrt{2}$ or ·46 times that of negative and positive ions.

The Formation of Complex Ions.

The method we used on p. 339 to calculate the rate of recombination of positive and negative ions can be applied to find the rate of combination of any two attracting systems A and B. We see that the expression (2) will always hold if d is defined to be the distance between the systems when the work required to separate them to an infinite distance starting from d is equal to the energy of a monatomic molecule at the temperature of the system.

There is an attraction between an ion and an uncharged molecule, and if the two combine, the result is a complex ion. We suppose that the attraction between an ion and a molecule follows the same law as that between an electric charge and a metallic sphere. If the distance between the charge and the centre of the sphere is r, the work required to separate them to an infinite distance is $e^2b^3/2r^4$, where b is the radius of the sphere and r is supposed to be considerably greater than b. Hence D, the value of d which occurs in the expression (2), p. 339, is given by

$$\frac{e^2b^3}{2\mathrm{D}^4} = \beta\theta.$$

Thus D varies as $\theta^{-1/4}$, while for the recombination of oppositely charged ions d varies as θ^{-1}.

At 0° C., $\beta\theta = e^2/4{\cdot}18 \times 10^{-6}$ cm., hence

$$2\mathrm{D}^4 = b^3 \times 4{\cdot}18 \times 10^{-6};$$

b will be of atomic dimensions ; we shall take it as 10^{-8}, with this value of b,

$$\mathrm{D} = 3{\cdot}8 \times 10^{-8}.$$

This is only about one-hundredth part of d for two oppositely

charged ions. The rate of combination of the ions with uncharged molecules at low pressures is thus

$$\pi\rho\sigma D^3 (U_i^2 + U_m^2)^{1/2} \left(\frac{1}{\lambda_i} + \frac{1}{\lambda_m}\right),$$

where ρ is the density of the ions, σ that of the uncharged molecules, U_i and U_m the average velocities of the ion and molecule respectively, and λ_i and λ_m their free paths.

The rate of combination between ions of opposite signs is

$$\pi\rho\rho' d^3 (U_i^2 + U_{i'}^2)^{1/2} \left(\frac{1}{\lambda_i} + \frac{1}{\lambda_{i'}}\right),$$

where ρ' is the density of the ions of opposite sign to those whose density is ρ, and d at 0° C. is $4{\cdot}18 \times 10^{-6}$.

Now, though d is very much greater than D (in the case we are considering d^3 is $10^6 D^3$) yet σ, the density of the uncharged molecules, is in general so much greater than ρ', the density of the ions, that σD^3 is greater than $\rho' d^3$. At atmospheric pressure σ is $2{\cdot}7 \times 10^{19}$, so that unless ρ' is greater than $2{\cdot}7 \times 10^{13}$, more ions at the beginning will unite with uncharged molecules to form complex ions than with ions of the opposite sign to form neutral systems. It requires very intense ionization to produce 10^{13} ions per c.c. at atmospheric pressure—far more intense than that produced by Röntgen rays of anything like normal intensity, though not more intense than that which frequently occurs in arcs and luminous electrical discharges; and unless the ionization has this high value, an ion will unite with an uncharged molecule to form a complex ion before it ends its career by combining with an ion of opposite sign.

The life of a complex ion may, however, be so short that the proportion of complex to free ions never exceeds a small fraction. Let us suppose that when there are p complex ions per unit volume, kp dissociate per second. Then

$$\frac{dp}{dt} = -kp + \pi\rho\sigma D^3 (U_i^2 + U_m^2)^{1/2} \left(\frac{1}{\lambda_i} + \frac{1}{\lambda_m}\right).$$

The maximum value of p/ρ is thus

$$\pi\sigma D^3 (U_i^2 + U_m^2)^{1/2} \left(\frac{1}{\lambda_i} + \frac{1}{\lambda_m}\right) \Big/ k.$$

We proceed to calculate the value of k; this value will depend upon the mechanism by which the dissociation of the complex ion is effected. We have not nearly as much direct information as is desirable on this point; there is one method, however, which it would seem must be operative,

though whether it is the only one at work is another question. This method is that of collision between complex ions and uncharged molecules. If, as the result of a collision between a complex ion and a molecule moving at high speed, more than a definite amount of energy is communicated to the complex ion, it will dissociate into a simple ion and an uncharged molecule. If a binary system A, B receive at a collision so much energy that

$$\frac{1}{2}\frac{M_A M_B}{M_A+M_B}(V_A^2+V_B^2-2V_A V_B\cos\theta)$$

is greater than the work required to separate A from B, the system will dissociate into A and B. In this expression M_A and M_B are the masses, V_A and V_B the velocities of A and B respectively, and θ the angle between V_A and V_B. The average value of $\cos\theta$ is zero, so that we may write the condition for dissociation as

$$\frac{1}{2}\frac{M_A M_B}{M_A+M_B}(V_A^2+V_B^2) > Q,$$

where Q is the work required to separate A from B. In the simple case where the complex ion is formed by a positively electrified molecule combined with an uncharged molecule of the same kind, $M_A=M_B$, and the condition for dissociation is

$$\frac{M_A}{4}V_A^2+\frac{M_B}{4}V_B^2 > Q,$$

or $T > 2Q$ if T is the kinetic energy of the complex ion.

Thus any collision which transfers to the complex ion more than 2Q units of kinetic energy will produce dissociation.

We have seen that the energy transferred at a collision between masses M and m is

$$\frac{4Mm}{(M+m)^2}T\sin^2\theta,$$

where θ depends on the geometry of the collision, *e. g.* the minimum distance between the bodies, as well as upon the law of force between M and m.

The maximum amount of energy which can be transferred at one collision is T, and this is only possible when $M_1=M_2$ and $\sin^2\theta=1$; in this case the bodies in collision exchange energies. When M_1 and M_2 are very different, only a small fraction of the energy is transferred at a collision. It must be remembered that, though when there is a smaller transference of energy at a collision, a molecule will gain less

energy when it collides with a faster molecule, yet it loses less when it collides with a slower; thus the limiting energy when it attains equilibrium will be independent of the fraction transmitted at each collision. The time taken to attain this state will depend upon the fraction of the energy transferred, and will diminish as the fraction increases.

To dissociate the molecule, 2Q units of energy must be gained.

Let us first take the case when the maximum amount is transferred at a collision: then the number of the complex ions dissociated per second is the number of collisions made by the complex ion with the molecules possessing more than 2Q units of kinetic energy.

Let u be the velocity of the complex ion; then assuming Maxwell's law for the distribution of velocities the number of molecules it meets per second having velocities between v and $v+dv$ and which are moving so that the perpendicular from the centre of the complex ion on the path of the centre of the molecule is between p and $p+dp$ is

$$4\left(\frac{h^3m^3}{\pi}\right)^{1,2} \mathrm{N}\, 2\pi p\, dp\, \epsilon^{-hmv^2}\, v^2 \mathrm{V}\, .\, dv,$$

where N is the number of molecules per unit volume, V the relative velocity of the complex ion and a molecule of the type we are considering:

$$\mathrm{V}^2 = u^2 + v^2 - 2uv\cos\phi, \quad . \quad . \quad . \quad . \quad (7)$$

where ϕ is the angle between u and v. When all directions of ϕ are equally probable, the chance that ϕ is between ϕ and $\phi+d\phi$ is $\frac{1}{2}\sin\phi\, d\phi$. The number of collisions where ϕ is between ϕ and $\phi+d\phi$ is thus

$$4\left(\frac{h^3m^3}{\pi}\right)^{1/2} \mathrm{N}\pi p\, dp\, \epsilon^{-hmv^2}\, v^2 \mathrm{V}\, dv \sin\phi\, d\phi,$$

but from (7)

$$\mathrm{V}\, d\mathrm{V} = uv\sin\phi\, d\phi,$$

so that

$$v^2 \mathrm{V}\sin\phi\, d\phi = \frac{v\mathrm{V}^2}{u}\, d\mathrm{V}.$$

Integrating with respect to V, and since v must be greater than u, the limits of V are $v+u$, $v-u$, the result is

$$\tfrac{2}{3}v\,(u^2+3v^2);$$

hence the number of collisions per unit time is got by integrating

$$4\left(\frac{h^3m^3}{\pi}\right)^{1/2} \mathrm{N}\pi p\, dp\, \epsilon^{-hmv^2} v^2_3(u^2+3v^2)\, dv,$$

where the limits of integration with respect to v are from $\frac{1}{2}mv^2=2\mathrm{Q}$ to $v=\infty$.

If the maximum transference of energy, *i. e.* T, occurs at each collision, the integral of this expression with regard to v, from $\frac{1}{2}mv^2=2\mathrm{Q}$ to $\frac{1}{2}mv^2=$infinity, will be the number of complex ions dissociated per second. If the energy transferred is only $\gamma\mathrm{T}$, then a single collision will not lead to dissociation unless $\gamma\frac{1}{2}mv^2=2\mathrm{Q}$. The number of collisions required when v^2 is less than this value will be proportional to $4\mathrm{Q}/mv^2$, so that the rate of dissociation will be reduced to the fraction $\gamma mv^2/4\mathrm{Q}$ of the value just given. Hence the number of complex ions dissociated in unit time is equal to

$$4\left(\frac{h^3m^3}{\pi}\right)^{1/2} \mathrm{N}\pi p\, dp\left[\int \epsilon^{-hmv^2} v\cdot\tfrac{2}{3}(u^2+3v^2)\gamma\frac{mv^2}{4\mathrm{Q}}\cdot dv + \int \epsilon^{-hmv^2} v^2_3(\mathrm{U}^2+3v^2)\, dv\right],$$

where the limits of the first integral are from

$$\tfrac{1}{2}mv^2=2\mathrm{Q} \quad \text{to} \quad \gamma\tfrac{1}{2}mv^2=2\mathrm{Q},$$

and for the second from

$$\gamma\tfrac{1}{2}mv^2=2\mathrm{Q} \quad \text{to infinity.}$$

In cases where there is appreciable combination, Q will be large in comparison with the energy due to thermal agitation; hence $h\mathrm{Q}$ will be large. Making the integrations and retaining only the terms which are most important when $h\mathrm{Q}$ is large, we find that the number of times each complex ion is dissociated per second is equal to

$$4\frac{(hm)^{1/2}}{\pi}\cdot \mathrm{N}\pi p\, dp\cdot\gamma\frac{4\mathrm{Q}}{m}\epsilon^{-4h\mathrm{Q}}$$

$$=4\left(\frac{1}{hm\pi}\right)^{1/2}\cdot \mathrm{N}\pi p\, dp\cdot 4\gamma h\mathrm{Q}\,\epsilon^{-4h\mathrm{Q}}.$$

If $\beta\theta$ is the average energy of a molecule at the absolute temperature θ due to the motion of its centre of gravity,

$$\beta\theta=\frac{3}{4h}.$$

and U_m, the average velocity of the molecules at the temperature θ, is equal to $2/(hm\pi)^{1/2}$; hence the number of times each complex ion is dissociated per second is

$$2U_m N\pi p\,dp\,.\,\gamma\frac{3Q}{\beta\theta}\epsilon^{-\frac{3Q}{\beta\theta}},$$

where

$$\gamma=\frac{4Mm}{(M+m)^2}\sin^2\theta.$$

If the collisions are like those between elastic spheres,

$$\sin^2\theta=1-\frac{p^2}{s^2},$$

where s is the sum of the radii of the colliding spheres. Substituting this value for γ and integrating from $p=0$ to $p=s$, we find that the number of times a complex ion is dissociated per second

$$=\frac{2Mm}{(M+m)^2}\pi Ns^2\,.\,U_m\frac{3Q}{\beta\theta}\epsilon^{-\frac{3Q}{\beta\theta}},$$

where m is the mass of a molecule, and M that of a complex ion. This is the value of k in the equation (see p. 353),

$$\frac{dp}{dt}=-kp+\pi\rho\sigma D^3(U_i^2+U_m^2)^{1/2}\left(\frac{1}{\lambda_i}+\frac{1}{\lambda_m}\right) \quad . \quad (8)$$

where p is the number of complex ions per unit volume.

Where M is not very different from m, the factor

$$\frac{4Mm}{(M+m)^2}N\pi s^2U_m$$

in k will be of the same order as the factor

$$(U_i^2+U_m^2)^{1/2}\left(\frac{1}{\lambda_i}+\frac{1}{\lambda_m}\right)$$

in the second term on the right-hand side of the equation; hence the value of p/ρ when things are in a steady state will be of the order

$$\frac{\pi\sigma D^3}{\frac{3Q}{2\beta\theta}\epsilon^{-\frac{3Q}{\beta\theta}}}.$$

At atmospheric pressure and room temperature, σ the number of molecules per cubic centimetre is $2{\cdot}7\times10^{19}$ and

(see p. 352) D is about 4×10^{-8}; hence $\pi\sigma D^3$ is about ·0054. Thus, unless the denominator in the expression for p/ρ is very small, the complex ions will only be a small fraction of the free ones.

The following table gives the values of $x\epsilon^{-x}$ for various values of x :—

x.	$x\epsilon^{-x}$.
4	·0732
5	·0336
6	·0148
7	·00637
8	·00266
9	·00110
10	·000453
12	$7{\cdot}4 \times 10^{-5}$

Hence there are about as many complex ions as free ones when $3Q/\beta\theta = 6$, and practically all the ions when $3Q/\beta\theta$ is greater than 12 are complex. Now, measured in volts $\beta\theta$ at 0° C. is about 1/30 of a volt; hence at this temperature practically all the ions will be complex if β, the work required to separate an ion from the molecule, is as great as 1/7 of a volt.

These complex ions in virtue of their electric charges will attract uncharged molecules and form ions of a still greater degree of complexity. We see from the preceding investigation that if p_n is the number per unit volume of complex ions which contain n molecules united to the original ion, then

$$\frac{dp_n}{dt} = -k_n p_n + a_n p_{n-1},$$

when k_n and a_n are quantities analogous to the k and $\pi\sigma D^3(U_i^2 + U_m^2)^{\frac{1}{2}}\left(\frac{1}{\lambda_1} + \frac{1}{\lambda_2}\right)$ in equation (2). The value of Q_n, the work required to separate a molecule from a complex ion, will diminish as n increases, and when it falls as low as a small multiple of 1/30 of a volt, the number of complex ions containing n or more molecules will be very small at 0° C. As long as Q_n is large compared with $\beta\theta$, we should expect the number of ions containing n molecules to increase with the value of n. Thus when complex ions are formed at all they will not be all of the same degree of complexity, but will include ions of different types. These different types will have different mobilities. Experiments on the mobilities of ions have failed to reveal the existence of more than one kind of positive ion, though Langevin's

method, which has been very frequently employed, is peculiarly suited to detect differences of mobilities. Even when a mixture of different gases of widely different densities is ionized by Röntgen rays, the positive ions as determined by their mobilities are all of one type. When we ionize a mixture of, say, hydrogen and methyl iodide, we do not find positive ions of large mobility corresponding to the hydrogen and others of smaller mobility corresponding to the methyl iodide—all the ions seem to have the same mobility. The reason for this will, I think, appear if we consider the times the ions exist in different states.

Life of a Free Ion.

Since the rate of combination of a simple ion with a molecule is (by p. 353)

$$\pi\sigma D^3\{U_i^2+U_m^2\}^{\frac{1}{2}}\left(\frac{1}{\lambda_i}+\frac{1}{\lambda_m}\right),$$

T the average time the ion exists in the free state is the reciprocal of this quantity, the distance the ion moves in this time is U_iT, and the number of free paths contained in this distance is U_iT/λ_i, or

$$\frac{1}{\pi\sigma D^3}\frac{U_i}{\{U_i^2+U_m^2\}^{\frac{1}{2}}}\frac{\frac{1}{\lambda_i}}{\frac{1}{\lambda_i}+\frac{1}{\lambda_m}}.$$

In the case of the positive ion, U_i and U_m will not be very different, and λ_i will be less than λ_m ; hence number of free paths will not be less than

$$\frac{1}{2\sqrt{2}.\pi\sigma D^3}.$$

Since $\pi\sigma D^3=\cdot0054$, the number of free paths described by the free ion before it unites with a molecule is about 60 at atmospheric pressure and 0° C. The free path of an ion will in consequence of the charge be somewhat less than that of an uncharged molecule. The free path in air at atmospheric pressure is 10^{-5} cm., so that the distance travelled by the ion in a free state will be somewhat less than 6×10^{-4} cm. As the average velocity of a nitrogen molecule is $4\cdot9\times10^4$, the time the ion is free is only about $1\cdot2\times10^{-8}$ second. This time will vary inversely as the square of the pressure, so that at a pressure of ·76 mm. of mercury the free ion would exist for 10^{-2} second. As the mobility of a positive ion in air at this pressure is about 1000 cm./sec., the ion could move under an electric

force of 1 volt per cm. through 10 cm. while in a free state. Thus, if the gas between two parallel plates at this distance apart were ionized at this pressure and an electric field of 1 volt per cm. maintained between the plates, the positive ions would be driven against the negative plate before they had united with molecules, so that the mobility determined under these conditions should be that of a simple ion and not that of a complex one. With weaker electric fields some of the ions would become complex before they reached the electrode. Their average mobility would thus be smaller than that under the more intense electric field.

Life of a Free Electron.

We saw (p. 351) that when the mass of one of the two combining particles is very small compared with the other, the rate of combination is

$$\pi\sigma D^3 (U_i^2 + U_m^2)^{\frac{1}{2}} \cdot \frac{1}{\lambda_i},$$

where λ_i is the free path and U_i the velocity of the smaller particle.

This represents the rate of combination of an electron with a molecule. Since U_i is very large compared with U_m, the rate is equal to

$$\pi\sigma D^3 \frac{U_i}{\lambda_i}.$$

T, the average life of an electron in a free state, is the reciprocal of this, $U_i T/\lambda_i$ is the number of free paths described by the electron in the state, so that this number is

$$\frac{1}{\pi\sigma D^3} = \frac{1}{\cdot 0054} = 170 \text{ at } 0^\circ \text{ C. and } 760 \text{ mm.}$$

Thus the electron describes about three times as many free paths as the positive ion; but whereas the energy free-path of a positive ion is of the same order as the geometrical free-path (*i. e.* $1/N\pi s^2$) of a molecule, the energy free-path of an electron is very much greater than its geometrical free-path.

The experiments of Herz and Townsend show that when a slowly-moving electron collides with a molecule of oxygen, it only loses a very small percentage of its energy; so that we may take the energy free-path to be of the order of 100 geometrical free-paths, and the path of the electron in a free

state of the order of 170×100, or 17,000 geometrical free-paths.

Loeb, who has made some very interesting determinations of the life of the free electron in oxygen, finds that it lasts for about 25,000 geometrical free-paths of the electron (Physical Review, xvii. p. 89) ; this is of the same order of magnitude as that just found.

From Loeb's result, since the velocity of an electron at 0° C. is about 10^7 cm./sec., we see that the life of a free electron in oxygen at atmospheric pressure is $25{,}000 \times 4 \times 10^{-5}/10^7$, or 10^{-7} second. At the pressure of ·76 mm. of Hg the time would be 1/10 of a second. As the mobility of the electron at this pressure is at least 2×10^5, the electron would under an electric field of a volt per cm. have time to describe 20,000 cm. before uniting with a molecule to form a complex ion. At the pressure of 7·6 mm. it could only describe 20 cm.

We have seen that at atmospheric pressure the life of a free ion is 10^{-8} for the positive ion and 10^{-7} or less for the electron. The time that a positive or negative charge exists, whether as a free or complex ion, before getting neutralized, is in general enormously longer than this. This time is equal to $1/\alpha n$, where α is the coefficient of recombination of the ions and n the number of ions per unit volume. It thus depends upon the intensity of ionization; but as with such intensities of ionization as are usually used in experiments on mobilities it would take at least a second for the ionization to sink to half-value after the ionizing agent has been cut off, the life of a charge must therefore be at least a second at atmospheric pressure, *i. e.* more than a million times that of a free ion.

The preceding calculation of the rate of combination of a free electron with an uncharged molecule is made on the supposition that it requires a finite amount of work to separate the electron from the molecule with which it is supposed to combine. There are, however, some molecules and even some atoms which cannot receive a negative charge. Thus, for example, when there are 8 electrons in the outer layer of an atom, as in neon and argon, the addition of another electron to the outer layer would produce an unstable system which would dissociate spontaneously. Evidence derived from the study of Positive Rays shows that though there are many molecules both of elements and compounds which cannot receive a negative charge, there are others, such as the molecules of hydrogen, carbon, and oxygen, which are able to do so, and it is to these that the preceding investigation applies.

Life of a Complex Ion.

We have calculated the rate at which ions are formed: we now proceed to consider the rate at which they disappear.

If p is number of complex ions and ρ that of free ions per unit volume when things have got into a steady state, then

$$\frac{p}{\rho} = \frac{\text{average life of a complex ion}}{\text{average life of a free ion}};$$

hence by equation (8), p. 357,

$$\text{average life of a complex ion} = \text{average life of a free ion} \times \frac{\pi\sigma D^3}{\epsilon^{-\frac{3Q}{\beta\theta}}} \cdot \frac{1}{3Q/2\beta\theta}.$$

At atmospheric pressure $\pi\sigma D^3 = \cdot 0054$, and the average life of both an electron and a free positive ion is of the order 10^{-7} second.

The following table gives the value of T, the average life of a complex ion, for different values of $3Q/\beta\theta$:—

$3Q/\beta\theta$....	5.	10.	15.	20.
T	$\cdot 086 \times 10^{-7}$	$5\cdot 8 \times 10^{-7}$	$5\cdot 8 \times 10^{-5}$	7×10^{-3}

Thus, until $3Q/\beta\theta$ approaches 20, the life of an ion in either the free or complex state is only a small fraction of a second. Hence, if the intensity of the ionization is such that the average life of a charge, *i. e.* the time which elapses before it combines with a charge of opposite sign, is as much as one second, the charge during its life will pass backwards and forwards between the free and combined states a large number of times. More generally, if more than one type of complex is possible, the charge will pass in its life through each of these types a large number of times, provided that for any one of these types $3Q/\beta\theta$ is not greater than 20.

In any experiments on ions, such as those on their mobility, if the ions are under observation for a period comparable with one second, the measurements obtained for any property will be the mean of those corresponding to various types of complex ions and not those corresponding to any one particular type. To be able to detect the different types of ions, we should have to employ methods where the times involved were comparable with the lives of the complex ions.

Chemical Combination.

We proceed to consider the application of principles similar to those we have been discussing to the general question of the combination of gases. Before chemical compounds are produced by the combination of two gases A and B, complexes containing the molecules of A and B in close proximity must be formed. We have seen, however, that unless the work required to separate the constituents in a pair of molecules is a considerable multiple of the energy corresponding to thermal agitation, very few such pairs will exist. The work required to separate at temperatures far above that of liquefaction two molecules of a gas will not in general be large compared with the energy of thermal agitation at those temperatures. If we take as the superior limit to the work required to separate two molecules the latent heat of vaporization of one gramme molecule divided by the number of molecules in a gramme molecule, the work required to separate two molecules of hydrogen is expressed by 1/100 of a volt, that required to separate two molecules of nitrogen by 1/16 of a volt, while the thermal energy at 0° C. is measured by 1/30 volt. Thus at this temperature the number of pairs of molecules of either hydrogen or nitrogen would be exceedingly small. Though the molecules of two gases may not be able to form pairs when the gases are pure, they may be able to do so when the gases contain ions. Complex ions will be formed: some of these will contain molecules of A, others molecules of B. If a complex positive ion containing a molecule of A unites with a negative one containing a molecule of B, an addition compound of A and B and the two simple ions will be produced. Again, a complex ion containing a molecule of A combined with a simple ion may form a still more complex one by uniting with a molecule of B, and in this way produce an addition compound of A and B and a simple ion; the life of this compound will be much shorter than that of one formed by two complex ions: on the other hand, the number of free molecules of B will in all probability be much greater than the number of complex ions; so that, though they will not last so long, more of the compounds containing a single ion will be formed. Though we should expect ions to be very efficient promoters of chemical combination, we must remember that in many cases where gases are ionized, *e. g.*, by Röntgen rays, the number of ions is such a minute fraction of the number of molecules that the amount of chemical action cannot be expected to be considerable, though it will be noticed that each ion may lead to

the formation of several molecules of the compound. There are, however, many instances of the effect of ions on chemical combination—such, for example, as the formation of new compounds such as ozone by what is known as the silent electric discharge. Again, Positive Ray Analysis shows that chemical action is very active in the negative glow in a discharge-tube.

A similar effect to that due to ions would occur if, instead of ions, molecules possessing a finite electrical moment, *i. e.* polar molecules, were mixed up with A and B.

These polar molecules exert on neighbouring molecules attractions greater than those exerted by non-polar molecules; so that, if P denotes a polar molecule, complexes (PA) and (PB) may be formed, though the number of pairs (AB) may be insignificant.

The molecules of the aggregates (PA) and (PB) will themselves be polar, and will therefore exert considerable attractions on each other and on simple molecules, the work required to separate them may be a considerable multiple of $\beta\theta$ the energy corresponding to thermal agitation; if this is so, the aggregates PA, B (PA, PB) will be produced in finite quantities. These aggregates are addition compounds of A and B and the polar molecules, so that polar molecules as well as ions may give rise to addition compounds.

The attraction between a polar molecule and a neutral molecule will be less than that between an ion and the molecule if the distance between them is the same; and if the ions were as numerous as the polar molecules, we should expect the former to be more effective in producing chemical combination. But while it is easy to get a large number of polar molecules, *e. g.* by the introduction of a little moisture, it is not, as we have already pointed out, at all easy to get anything like the same number of ions; so that the effect of polar molecules may, as in the experiments of Professor Baker, be more conspicuous than that of ions.

Though ions and polar molecules may in this way lead to the formation of addition compounds, it does not follow that the formation of these compounds would necessarily be followed by that of a true valency compound of A and B. Before two molecules A and B in close proximity can form such compounds, it may be necessary to do work on A and B before the atoms can rearrange themselves in the way necessary for the formation of such a compound. Thus, for example, though in the combination of H_2 and Cl_2 a great deal of work is given out when 2HCl has once been formed, yet before the rearrangement of the atoms necessary

for this can occur, work may have to be supplied to split up the H_2 and Cl_2 molecules : a catalyst which will either wholly supply this work or diminish the amount materially may be required. It is important to notice that ions and polar molecules, besides promoting the formation of addition compounds, may themselves act as catalysts. Thus, for example, the presence of an electron or the negative end of a polar molecule near the positive end of the system A—A will diminish the work required to move A_+ from A_-, promoting the rearrangement of the atoms in the A molecule and thus acting as a catalyst.

Thus the presence of either charged ions or polar molecules does two things, each of which promotes chemical combination :—

(1) It promotes the formation of addition compounds.
(2) The ions and polar molecules act like a catalyst in helping the rearrangement of the atoms necessary to convert the addition compound into the final chemical one.

To form some estimate of the rate at which chemical combination might be expected to occur under the influence of ions and polar molecules, we may proceed as follows :—

Let us take the case when, as in the union of hydrochloric acid gas and ammonia, one molecule of a gas A unites with one of a gas B to form a molecule of the compound.

Let (A), (B) be the number of A and B molecules respectively per unit volume ;

(p) the number of ions or polar molecules per unit volume ;

(pA) the number of complexes per unit volume of an ion or polar molecule with a molecule of A.

The addition compounds of A and B due to the ions may be of the type $\{(p\mathrm{A})(p\mathrm{B})\}$ or $\{(p\,.\,\mathrm{A})(\mathrm{B})\}$.

We shall suppose that addition compounds pass immediately into chemical compounds, and that these when once formed do not decompose ; so that the rate of formation of these additive compounds is the same as that of the chemical one.

Since the addition compound is supposed not to dissociate,

$$\frac{d}{dt}(p\mathrm{A}\,.\,p\mathrm{B}) = a(p\mathrm{A})(p\mathrm{B}) \quad . \quad . \quad . \quad . \quad (9)$$

and

$$\frac{d}{dt}(p\mathrm{A},\,\mathrm{B}) = a'(p\mathrm{A})(\mathrm{B}), \quad . \quad . \quad . \quad . \quad (10)$$

where a and a' are the coefficients of combination of pA and pB and of pA and B respectively.

Now a and a' are of the form (see p. 339)

$$\pi d^3 . (u^2 + u_1^2)^{1/2} \left(\frac{1}{\lambda} + \frac{1}{\lambda'}\right).$$

This in a gas at atmospheric pressures and temperatures is of the *order*

$$\pi d^3 \times 10^9.$$

d is the distance between the two combining molecules when the work required to separate them is equal to the energy of thermal agitation ; if one of these molecules has a positive and the other a negative charge, as in the addition compound formed by complex ions, then (see p. 339)

$$d = 4{\cdot}18 \times 10^{-6} \quad \text{and} \quad \pi d^3 \times 10^9 = 2{\cdot}3 \times 10^{-7}.$$

If all the ions are complex, and if there as are many A molecules as B and the free ions distribute themselves equally between A and B, then

$$(p\mathrm{A})_+ = (p\mathrm{A})_- = (p\mathrm{B})_+ = (p\mathrm{B})_- = \tfrac{1}{4}p$$

and (9) becomes

$$\frac{d}{dt}(p\mathrm{A} . p\mathrm{B}) = \frac{a}{16} p^2 = \frac{2{\cdot}3}{16} \times 10^{-7} p^2.$$

If there is one ion for every million molecules, then at atmospheric pressure and 0° C.

$$p = 2{\cdot}7 \times 10^{13},$$

$$\frac{d}{dt}(p\mathrm{A} . p\mathrm{B}) = 1{\cdot}03 \times 10^{19}.$$

Now there are only $1{\cdot}35 \times 10^{19}$ molecules of A and B per unit volume, so that with this rate combination would be complete in a time comparable with one second. We could not, however, get ionization approaching this in intensity except in intense electrical discharges through gases. For ionization by Röntgen rays one ion per 10^{10} molecules would be a high estimate, and in this case it would take a time comparable with 10^8 second, or more than three years, for the combination to be complete.

When the addition compound is $(p\mathrm{A} . \mathrm{B})$, the value of d is 4×10^{-8} (see p. 352) and $\pi d^3 = 2 \times 10^{-22}$, hence a' is of the order 2×10^{-13} ; and if all the ions are complex $(p\mathrm{A}) = p/4$; and

$$\frac{d}{dt}(p\mathrm{A} . \mathrm{B}) = {\cdot}5 \times 10^{-13} p(\mathrm{B}).$$

If there is one ion per million molecules and the gas is at atmospheric pressure,

$$p = 2{\cdot}7 \times 10^{13},$$

$$(\mathrm{B}) = \tfrac{1}{2} \times 2{\cdot}07 \times 10^{19};$$

so that

$$\frac{d}{dt}(p\mathrm{A}.\mathrm{B}) = 1{\cdot}4 \times 10^{19},$$

and the combination would be complete in less than one second; if there was one ion per 10^{10} molecules, the combination would be complete in about 3 hours.

Let us now pass on to the case when instead of ions we have polar molecules. If m is the electrostatic moment of a molecule, the work required to separate two such molecules separated by a distance r is m^2/r^3, or if $m = e \times 10^{-8}$, $e^2 \times 10^{-16}/r^3$; hence d will be given by

$$\frac{e^2 \times 10^{-16}}{d^3} = \beta\theta,$$

$$= \frac{e^2}{4{\cdot}18 \times 10^{-6}} \text{ at } 0^\circ \text{ C.}$$

So that

$$d^3 = 4{\cdot}18 \times 10^{-22}$$

and $$\pi d^3 \times 10^9 = 1{\cdot}3 \times 10^{-12}.$$

Thus

$$\frac{d}{dt}(p\mathrm{A}.p\mathrm{B}) = 1{\cdot}3 \times 10^{-12} \times (p\mathrm{A})(p\mathrm{B}).$$

We have to remember that in general a large proportion of polar molecules are free and uncombined. Let us suppose that only one per cent. are combined, and that those which are combined are distributed equally between A and B, so that $(p\mathrm{A}) = p/200 = (p\mathrm{B})$; then

$$\frac{d}{dt}(p\mathrm{A}.p\mathrm{B}) = \frac{1{\cdot}3}{4} \times 10^{-16} p^2.$$

If there is one polar molecule to 10^4 of the others, $p = 2{\cdot}7 \times 10^{15}$, so that

$$\frac{d}{dt}(p\mathrm{A}.p\mathrm{B}) = 2{\cdot}37 \times 10^{14},$$

a rate which would make the combination complete in a little over a day.

When the addition compounds are of the form $(p\mathrm{A}, \mathrm{B})$, since the work required to separate an electric doublet whose

moment is m from an uncharged molecule of radius b is of the order

$$\left(\frac{m}{r^3}\right)^2 \tfrac{4}{3}\pi b^3,$$

if d is the distance when this work is equal to the thermal energy at 0° C., then

$$\left(\frac{m}{d^3}\right)^2 \tfrac{4}{3}\pi b^3 = \beta\theta = \frac{e^2}{4{\cdot}18\times 10^{-6}}.$$

m will be of the order $e\times 10^{-8}$ and b of the order 10^{-8}; so that

$$d^6 = 4{\cdot}2\times 4{\cdot}18\times 10^{-46}$$

or

$$\pi d^3 = 1{\cdot}26\times 10^{-22}.$$

Hence

$$\frac{d}{dt}(p\mathrm{A}\,.\,\mathrm{B}) = 1{\cdot}26\times 10^{-13}\times(p\mathrm{A})\mathrm{B}.$$

If one in a hundred of the polar molecules are combined with the other molecules, $(p\mathrm{A}) = p/200$. Hence at atmospheric pressure, if there is one polar molecule for 10^4 combining molecules,

$$(p\mathrm{A}) = 1{\cdot}35\times 10^{13}, \qquad \mathrm{B} = 1{\cdot}35\times 10^{19},$$

and

$$\frac{d}{dt}(p\mathrm{A}\,.\,\mathrm{B}) = 2{\cdot}3\times 10^{19};$$

so that the combination would be complete in about one second. If there were only one polar molecule in a million of the others, the combination would be complete in about a minute. These numbers illustrate the enormous effect of traces of polar molecules on chemical combination.

Velocity of Monomolecular Reactions.

The investigation we gave for the rate of dissociation of a complex ion would apply to the dissociation of any gaseous molecule if this is due to molecular impacts. In this case, if

$$\frac{d\mathrm{P}}{dt} = -k\mathrm{P},$$

k is of the form

$$\frac{\mathrm{Q}}{k\theta}\frac{\mathrm{U}_m}{\lambda}\epsilon^{-\frac{\mathrm{Q}}{\mathrm{R}\theta}}, \qquad (11)$$

where θ is the absolute temperature, Q the energy required

to dissociate the molecule, U_m the mean velocity of the molecules at the temperature θ, and λ the mean free path of the molecule ; U_m/λ is the reciprocal of the time of relaxation of the gas, and is proportional to the pressure.

The subject of monomolecular reactions has excited a good deal of attention, and expressions for the rate have been published by Dushman (Journal of the Franklin Institute, clxxxix. p. 515), Trautz (*Zeitsch. für Physik*, xi. p. 113, 1920), Rice (Phil. Mag. xlvi. p. 312), and McKeown (Phil. Mag. xlvi. p. 321). A general account of what has been done in this subject, together with a bibliography, is given by Harned (Proc. Franklin Inst., Aug. 1923). None of these authors, however, attributes the dissociation to molecular impacts ; in fact, the laws of dissociation have been supposed to rule this explanation out of court. I pointed out in my 'Applications of Dynamics to Physics and Chemistry,' p. 201 (1888), a difficulty which is met with by supposing that the decomposition of gaseous molecules is due to collision. This may be put as follows :—If m is the number of undissociated molecules, k_1 the rate of dissociation, n the number of atoms, k_2n^2 their rate of combination, then when things are in a steady state

$$k_1m = k_2n^2.$$

It follows from thermodynamical principles that m/n^2 is not affected by the presence of a neutral gas; but if the dissociation is due to molecular impacts, k_1 will be increased by the introduction of an inert gas, for the number of impacts will be increased, and *if the presence of the inert gas does not increase the number of combinations*, n^2/m would be increased, which is not the case. The argument is sound if the statement in italics is true. We have seen, however, in the discussion of the rate of recombination of gaseous ions that this rate is affected by the pressure of the gas, and that when this pressure is not too high the rate is directly proportional to the pressure, and this result is confirmed by Thirkill's experiments on the rate of recombination of ions. This result ought to apply, if the theory is correct, to all cases of gaseous recombinations which occur in the body of the gas and not on the sides of the vessel in which the gas is contained.

The rate of recombination of dissociated atoms would be increased by the presence of a neutral gas; thus k_2 will be increased, and if n^2/m is to remain constant, k_1 must increase too, as it would do if the dissociation were due to collisions. Thus the laws of dissociation support the view that the dissociation is due to collisions.

Professor Perrin (*Ann. de Chemie et de Physique*, xi. p. 5) quotes the absence of appreciable electrical conductivity in many cases of chemical combination as an objection to the view that ionization is due to collisions, for we know from experiments on Positive Rays that rapidly-moving molecules ionize by collision the gas through which they are moving. It is known, however, that this ionization does not take place to any appreciable extent unless the energy of the moving molecules exceeds a critical value which is very high (the lowest value yet found by experiment corresponds to 300 volts, which is far in excess of the energy required to dissociate a molecule into neutral atoms).

Experiments have been made to test the truth of various expressions for the rate of monomolecular reactions: the dissociation of phosphine (Trautz, *Zeitschrift Anorg. Chem.* cvi. p. 95, 1919), H_2, I_2, Br_2, Cl_2 (Dushman, *loc. cit.*), have been used for this purpose. It must, however, be noted that when $Q/R\theta$ is large, as it is for all these gases, the factor $\epsilon^{-Q/R\theta}$ which occurs in all the expressions for k so dominates its value that a small percentage change in the value assigned to Q would more than cover the differences in the other factor occurring in the value of k given by different writers. A more searching test would be to find the values of k at a given temperature for I_2 or N_2O_4 when these gases are mixed with inert gases at different pressures, care being taken that the effects due to the walls of the vessel are eliminated. Experiments with this object are in progress at the Cavendish Laboratory.

From equation (11) we have, since U_m varies as $\theta^{\frac{1}{2}}$,

$$\frac{d\log k}{d\log\theta} = \frac{Q}{R\theta} - \frac{1}{2}.$$

Since $Q/R\theta$ is large, this is a close approximation to the empirical formula given by Arrhenius:

$$\frac{d\log k}{d\log\theta} = \frac{Q}{R\theta}.$$

When the substance concerned in the monomolecular reaction is a solid and not a gas—as, for example, in the problem of the rate of sublimation of a solid—we cannot suppose that impacts between the molecules are the cause of the transference of large quantities of energy to the molecules which are liberated from the solid. We can, however, on lines analogous to those used for gaseous reactions, obtain an expression for k.

The molecules of a solid are arranged along lattices, and if one of the molecules is struck, a pulse will spread through the system, displacing the molecules as it passes over them. Thus we may regard the solid as the seat of a very large number of pulses which are continually displacing the molecules from their equilibrium positions. These pulses are so numerous that each molecule is affected by a very large number of them simultaneously, and the phases of the different pulses are arbitrarily distributed. Thus the effect of these pulses on the displacement of a molecule will be obtained by the same rule as that which gives the resultant of a large number of displacements of arbitrary phase. This problem was solved by Lord Rayleigh ('Theory of Sound,' 2nd edit. vol. i. p. 42), who showed that the probability of the amplitude being between r and $r+dr$ was in the three-dimensional problem

$$3\sqrt{\frac{6}{\pi n^3}}\epsilon^{-r^2/\frac{3}{2}n}r^2dr, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where n is the mean value of r^2.

The energy of the molecule is proportional to r^2, and if we assume that the mean energy of the molecules is as in a gas proportional to the absolute temperature and denote as in a gas 2/3 of this energy by $R\theta$, the probability of a molecule having energy between T and $T+dT$ is, from (12),

$$2\sqrt{\frac{1}{\pi(R\theta)^3}}\epsilon^{-T/R\theta}\sqrt{T}\,.\,dT.$$

The probability of a molecule having energy greater than Q is therefore

$$2\sqrt{\frac{1}{\pi(R\theta)^3}}\int_Q^\infty \epsilon^{-T/R\theta}\sqrt{T}\,.\,dT.$$

An approximate value of the integral when $Q/R\theta$ is large is

$$R\theta\,\epsilon^{-Q/R\theta}\sqrt{Q};$$

so that the probability of the molecule having energy greater than Q is approximately

$$\frac{2}{\sqrt{\pi}}\epsilon^{-Q/R\theta}\left(\frac{Q}{R\theta}\right)^{\frac{1}{2}}. \quad . \quad . \quad . \quad . \quad (13)$$

It should be mentioned that this result does not depend upon all the impulses having the same intensity; it holds when the pulses have different intensities, provided there

are always enough of each type acting on a molecule to justify the employment of statistical methods.

If Q is the work required to separate the molecule from the solid, (13) will give the probability of a molecule at the surface being in a condition to escape from it. To find the rate at which they escape, we must find the rate at which the supply of these active molecules is renewed.

It is evident that after a time equal to that which a pulse requires to travel over a distance equal to its thickness, the distribution of resultant intensities will change entirely: the molecules which at first were at places where the superposition of the pulses was such as to give a large resultant will no longer do so; on the other hand, some molecules which are at places where the resultant amplitude had previously been small will now find themselves vibrating with a larger amplitude. Thus T, the time taken by a pulse to pass over a distance equal to its thickness, is the average time taken by the molecules which are in a particular state with respect to energy to change into another state. Thus, if P is the number of molecules which have energy greater than Q, P/T will be the number which pass out of this state per second, and this when things have settled down into a steady condition will be the number which in one second acquire energy greater than Q. Hence, if N be the number of molecules, the number that pass per second into a state where the energy is greater than Q is

$$\frac{1}{\mathrm{T}}\frac{2\mathrm{N}}{\sqrt{\pi}}\left(\frac{\mathrm{Q}}{\mathrm{R}\theta}\right)^{\frac{1}{2}}\epsilon^{-\mathrm{Q}/\mathrm{R}\theta}.$$

So that

$$k=\frac{1}{\mathrm{T}}\frac{2}{\sqrt{\pi}}\left(\frac{\mathrm{Q}}{\mathrm{R}\theta}\right)^{\frac{1}{2}}\epsilon^{-\mathrm{Q}/\mathrm{R}\theta}.$$

To determine the value of T, we notice that pulses of the kind we are considering will not only excite the motion of the molecules, but will also start pulses of radiation of the same duration. All bodies give out a continuous spectrum in which λ_m, the wave-length where the energy is a maximum, is by Wien's law inversely proportional to the absolute temperature and at 0° C. is about 10^{-3} cm. If we regard this light radiation as made up of pulses, λ_m will be a measure of the average thickness of the pulse and λ_m/c, if c is the velocity of light, will be the duration of the effect which gave rise to the pulse. If we suppose that the radiation arises from the pulses of molecular displacement, this will be equal to T, so that $\mathrm{T}=\lambda_m/c$.

Thus k, the rate of monomolecular reaction in a solid, will be given by the equation

$$k = \frac{c}{\lambda_m} \frac{2}{\sqrt{\pi}} \left(\frac{Q}{R\theta}\right)^{\frac{1}{2}} \epsilon^{-Q/R\theta}.$$

Since λ_m is inversely proportional to θ,

$$\frac{d \log K}{d \log \theta} = \frac{Q}{R\theta} + \tfrac{1}{2}.$$

The value of k for a solid bears to that for a gas, Q and θ being the same for the gas and solid, the ratio of

$$\frac{c}{\lambda_m} \text{ to } \left(\frac{Q}{R\theta}\right)^{\frac{1}{2}} \frac{U_m}{\lambda},$$

where λ is the mean free path of a molecule and not a wave-length.

Since at 0° C. $c/\lambda_m = 3 \times 10^{13}$ and U_m/λ is of the order 10^9 at 760 mm., we see that unless $Q/R\theta$ is exceptionally large, or the pressure of the gas very high, the value of k for a solid will be considerably greater than that for a gas.

Influence of the Walls of the Vessel on Gaseous Reactions.

The expression we have deduced for the rate of gaseous reactions is founded on the assumption that these take place in the body of the gas. Van't Hoff long ago showed that the walls of the vessel in which the gas is contained often exert great influence on the velocity of the reaction. A very striking instance of this effect is given by Bodenstein (*Zeitsch. f. Physik. Chem.* xxix. p. 689), who found that the combination of hydrogen and oxygen at the temperature of 600° occurred entirely at the surface of the vessel in which the gases were contained.

The conditions for chemical combination at a surface are quite different from those for the body of the gas. It would seem that the first stage towards the union of two atoms or molecules A, B would be for these to form molecular compounds with the molecules at the surface, and give rise to a surface layer of molecules which may be denoted by SA, SB. SA and SB then form addition compounds, from which AB is deposited on the surface; it may subsequently evaporate and find its way to the body of the gas.

With regard to the formation of SA, SB, the molecules of the solid are so close together that the opportunities of getting rid of superfluous energy are great enough to make almost

every molecule which strikes against the surface form a molecule compound with it if it is clean.

Thus the rate of formation of these molecular compounds will not be affected by the pressure of the inert gas, nor will the rate of formation of the addition compounds formed from the systems SA, SB condensed on the surface. Again, the rate at which AB evaporates from the surface will be expressed by a formula similar to that for the evaporation of a solid. Thus in this case the only way an inert gas can affect the rate of the chemical reaction is by forming a layer on the surface of the solid and protecting it from the action of A and B. This would retard the combination, while for reactions in the body of the gas the effect of the inert gas would be acceleration. Thus it is necessary in studying gaseous reactions to separate the part occurring on the surface from that occurring in the body of the gas.

Another view of the origin of monomolecular reactions is that they are due to radiation. The energy in the black body radiation at θ with a frequency between ν and $\nu + d\nu$ is proportional to

$$\nu^2 \frac{h\nu/\mathrm{R}\theta}{\epsilon^{h\nu/\mathrm{R}\theta} - 1} \cdot d\nu,$$

or, if $h\nu/\mathrm{R}\theta$ is large, to

$$\nu^2 \cdot h\nu/\mathrm{R}\theta\, \epsilon^{-h\nu/\mathrm{R}\theta} d\nu.$$

If the monomolecular reaction was due to radiation within a small range of frequency—fixed for each substance—and proportional to the energy of this kind of radiation, the expression for the rate would contain the factor $\epsilon^{-h\nu/\mathrm{R}\theta}$, and if ν were determined by the quantum relation

$$\mathrm{Q} = h\nu,$$

this factor would become $\epsilon^{-\mathrm{Q}/\mathrm{R}\theta}$, which is the law indicated by experiment. This view is, however, open to very serious objection, for, as Professor Lindemann has pointed out, the intensity of the radiation may by artificial illumination be increased many thousandfold without any commensurate increase in the rate of the reaction. It is not, as we have seen, necessary to have recourse to radiation to get the factor $\epsilon^{-\mathrm{Q}/\mathrm{R}\theta}$ in the expression for the rate of radiation.

The expressions for the velocity of chemical reactions illustrate and explain the enormous influence of water-vapour, of surface effects, of impurities, of catalysts generally

upon the progress of chemical combination. For these expressions for the rate of the reaction contain as a factor $\epsilon^{-Q/R\theta}$, where Q is the work required per molecule to bring the substance from the initial to the final state. When Q is large compared with $R\theta$, this factor is exceedingly small.

If the circumstances are such as to admit of the transition from the initial to the final stage taking place in two stages instead of one, the velocity of the reaction may be increased enormously. To take an example: suppose the complete reaction involved a value of Q represented by two volts, the factor $\epsilon^{-Q/R\theta}$ would at 0° C. be equal to ϵ^{-60}; if, however, the change took place in two stages, the factor $\epsilon^{-Q/R\theta}$ for each stage would be ϵ^{-30} (supposing the energy changes to be equally divided between the two stages). Now ϵ^{-30} is about 10^{13} times ϵ^{-60}, so that the velocity of the reaction would be increased more than a billion times by dividing it into two stages.

The effect of polar molecules, of free surfaces, of impurities, &c. is to provide opportunities for the formation of phases intermediate between the initial and final one, such that the transference from one phase to the next requires the expenditure of much less energy than that from the initial to the final one. These small energy changes go on with so much greater rapidity than the large one, that though several are required to complete the change from the initial to the final state, this is overbalanced to an overwhelming extent by the much greater rapidity of the individual changes.

To take an example: if the reaction we are considering is the dissociation of AB into A and B. If polar molecules such as those of water are present, the addition compound represented by $H_2O(AB)H_2O$ might be formed; this could dissociate (1) into H_2O . A and H_2O . B, and (2) these again into A, B, and H_2O. If each of the changes (1) and (2) required less energy than the direct change AB = A + B, the rate of dissociation would be increased greatly by the presence of the polar molecules.

A similar effect might be produced by a surface on which AB could condense, forming addition compounds with the molecules at the surface, which we may denote by S . AB . S; these may dissociate into SA, SB, and these again into A, B, S.

The formation of these intermediate compounds may so accelerate the rate of reaction, that the difference between effects when they are present and when they are absent may be so large as to justify the statement that the presence of

the agents which produce these intermediate compounds is necessary for the chemical reaction.

As the effects produced are so large, a very small quantity of these intermediate compounds may produce a very pronounced effect on the reaction.

It is necessary to be alive to the fact that even when we are dealing with such an apparently simple case as a monomolecular reaction the actual processes involved may be much more complex than those which appear on the surface. Thus, for example, the reaction investigated by Cohen on the decomposition of As. H_3 by heat (*Zeitsch. Physik. Chem.* xxv. p. 483) is often cited as a proof that gaseous dissociation cannot be produced by collision, since Cohen found that it was not measured by the presence of a neutral gas. It is probable, however, that the dissociation took place at the sides of the vessel, since the nature of these surfaces had a great effect on the velocity of the reaction. If this is so, we should not expect the rate to be affected by the presence of a neutral gas, and the experiments do not touch the question whether or not collisions may in certain cases produce dissociation.

Summary.

The paper contains investigations—

(1) On the rate of recombination of positive and negative ions, it is shown that the coefficient α is, at not too high pressures, given by the equation

$$\alpha = \pi d^3 (U_+^2 + U_-^2)^{\frac{1}{2}} \left(\frac{1}{\lambda_+} + \frac{1}{\lambda_-} \right),$$

and at high pressures by

$$\alpha = 2\pi d^3 (U_+^2 + U_-^2)^{\frac{1}{2}},$$

where d is given by the equation $e^2/d = \beta\theta$, where $\beta\theta$ is the energy of an atom of a monatomic gas at the absolute temperature θ, U_+ and U_- the average velocities of the polar and negative ions, λ_+ and λ_- the energy free-paths of these ions. It follows from these expressions that when the pressure is low, α is proportional to the pressure, which is in accordance with Thirkill's experiments. At higher pressures α should be independent of the pressure. The numerical value

for α for air at 0° C. and 760 mm. given by the preceding expression is in very fair agreement with the value found by observation.

(2) The values for λ_+ and λ_- are not the same as λ for an uncharged molecule : it is shown that λ_+/λ is a function of $(w/\beta\theta)^{\frac{1}{3}}$, where $\beta\theta$ is the same as before and w is the work required to separate a charged ion from an uncharged molecule with which it is in contact.

(3) When the negative charge is carried by electrons, special consideration is required in consequence of the disproportion between the masses of the electron and the molecules with which it comes into collision. It is shown that the energy free-path of an electron is exceedingly long, unless the energy of the electron when in collision with an electron in a molecule of the gas is comparable with the ionizing potential of the gas.

An expression is found for the rate of recombination of an electron and a positive ion.

(4) The rate of formation of complex ions is investigated, as well as the proportion between simple and complex ions when the gas is in a steady state. It is found that the condition that the ions should be mainly complex is the same as that for the free-path of an ion being much less than that of an uncharged molecule. Expressions are found for the periods which elapse before a simple positive ion becomes a complex one or an electron becomes a negative ion : the values obtained for the latter are of the same order as those found by Loeb in his experiments on this point.

(5) In the latter part of the paper the same principles are applied to Chemical Combination. Expressions are found for the rate at which two gaseous systems A and B combine, and also for the rate at which the compound AB dissociates. If p and q are the number of units of A and B respectively in unit volume, αpq the number which recombine per second, α is given by an expression of the same form as that for the coefficient of recombination of positive and negative ions, and at not too high pressures is proportional to the pressure. The rate of decomposition of the gaseous compound AB is determined on the hypothesis that it is due to collisions with the molecules of the gas ; the objections which have been urged against this type of dissociation are shown not to be valid when the combination takes place in the way we have supposed.

(6) The effect of polar molecules in hastening chemical

combination by promoting the formation of polar molecules is investigated and found to be very large.

(7) An expression for the rate of monomolecular reactions in solids such as that of sublimation is obtained, and the great influences of surfaces such as the walls of the vessel in which the gas is contained on the rate of chemical reaction is indicated by the investigation.

Monomolecular reactions are regarded as due to the accumulation of thermal energy in particular molecules until these have sufficient energy to dissociate or evaporate as the case may be. Maxwell's law of the distribution of energy among the molecules of a gas expresses the fact that owing to collisions the energy accumulates in some molecules until it reaches a value far above the normal, though naturally the number of molecules which have energy much in excess of the normal diminishes rapidly as the excess increases. In gases the accumulation of energy is due to the collision among the molecules of the gas. In solids where the molecules form connected space-lattices the transference and accumulation of energy is due to pulses of displacement of molecules travelling in great number through the solid and producing by superposition effects whose magnitudes are governed by the same principles as those which determine the resultant amplitude of a large number of vibrations of arbitrary phase.

The expression for the rate of the monomolecular reaction contains two factors, one expressing the number of molecules which have the energy necessary for the change : this factor is of the form $\epsilon^{-Q/R\theta}$, where Q is this energy and θ the absolute temperature ; the other factor expresses the rate at which molecules enter or leave the state. In gases this rate is inversely proportional to the time between two collisions, *i. e.* directly proportional to the number of collisions made by a molecule per second ; in air at 0° C. and 700 mm. pressure this would be of the order 5×10^9. In solids the time concerned is the duration of the passage of a pulse of light whose thickness is 10^{-3} cm. at 0° C. over a molecule ; this is $1/3 \times 10^{13}$ seconds, and the rate factor is 3×10^{13} : thus these reactions would tend to go on much more rapidly at the surface of solids than in the body of a gas.

XXX. *The Motion of Electrons in Neon*, *By* V. A. Bailey, *M.A., D.Phil., Oxford, Associate Professor of Physics, University of Sydney**.

1. In the account of experiments on the motion of electrons in argon and in helium recently published in the Philosophical Magazine † by Professor Townsend and myself, we gave a description of the methods used to investigate these gases. The same apparatus has now been used for the investigation of the behaviour of electrons in neon.

A quantity of neon containing about 1 per cent. of helium was very kindly supplied by M. Georges Claude, of Paris. No attempt was made to remove any of the helium, as this requires the use of liquid hydrogen, but all the common impurities were removed by passing the gas over charcoal at liquid-air temperature, before admitting it into a glass reservoir.

The measuring apparatus was tested for gas-tightness over a period of four weeks and found to have no perceptible leak in that time.

It was considered advisable to purify the gas again by passing it through a small charcoal tube interposed between the reservoir and the measuring apparatus and immersed in liquid air. The gas was generally kept in contact with the charcoal for about an hour before being admitted to the apparatus.

The same precautions as before were taken to prevent access of mercury vapour to the measuring chamber.

2. The experimental results are given in Table I., with the following notation :—

p the gas pressure in millimetres of mercury,

Z the electric force in volts per centimetre,

W the velocity of the electrons in the direction of the electric force, in centimetres per second,

k the factor by which the energy of agitation of the electrons exceeds that of an equal number of gas molecules at 15° C.

* Communicated by Prof. J. S. Townsend, F.R.S.

† Phil. Mag. Nov. 1922 and Oct. 1923.

TABLE I.

p.	Z.	Z/p.	k.	W$\times10^{-5}$.
80	4·28	·0535	21·2	3·25
80	6·4	·08	29·5	3·50
80	8·56	·107	36·6	4·08
80	17·1	·214	65·3	5·10
40	8·55	·214	66·5	5·12
80	25·5	·32	93·5	...
80	34·2	·428	119	...
40	17·1	·428	122	6·55
40	25·5	·64	167	8·1
37	25·5	·69	180	...
40	34·4	·86	198	10·3
20	17·2	·86	183	...
20	25·8	1·29	225	16·5
20	34·3	1·72	264	22·9
10	17·2	1·72	234	...
10	34·3	3·43	304	46·0
5·05	17·0	3·36	258	...
5·15	34·3	6·67	320	81·0
2·5	17·0	6·8	310	...

Each of these results is the mean of several determinations made with different samples of the gas, the following set being typical :—

p.	Z.	Z/p.	k.	W$\times10^{-5}$.
80	17·2	·215	66·7	5·35
80	17·2	·215	63·0	5·18
80	17·2	·215	64·5	5·04
80	17·0	·212	65·4	5·05
80	17·0	·212	66·6	4·90

The method of determining k and W is illustrated by the following example, the electrodes on which the stream of electrons was received being arranged as shown in figs. 1 and 2 in the paper on argon *. For $p=80$ and $Z=17$ it was found that the fraction $R=·329$ of the stream of electrons settled on the middle electrode, and that a magnetic force of strength $H=250$ was necessary to divert the centre

* Phil. Mag. Nov. 1922, p. 1035.

Fig. 1.

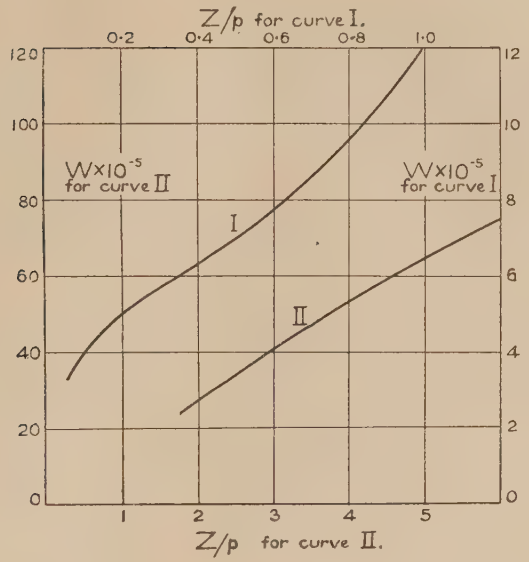
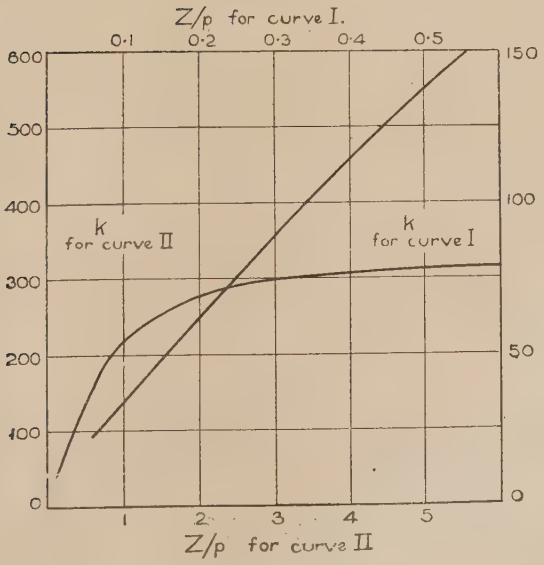

Z/p for curve I.
0·2
0·4
0·6
0·8
1·0
120
100
80
60
40
20
0
12
10
8
6
4
2
0
W×10⁻⁵ for curve II
W×10⁻⁵ for curve I
I
II
1
2
3
4
5
Z/p for curve II.

Fig. 2.


Z/p for curve I.
0·1
0·2
0·3
0·4
0·5
600
500
400
300
200
100
0
150
100
50
0
k for curve II
k for curve I
1
2
3
4
5
Z/p for curve II

of the stream to the nearer air-gap. From the Standard Distribution Curve * it is seen that the ratio Z/k has the value ·260 for R=·329, so the value of k is determined to be 65·4. The velocity W is calculated by means of the formula $WH/Z=\tan\theta$, θ being the angle of deflexion of the stream due to the magnetic force H. Preliminary experiments having given the value ·0742 for $\tan\theta$, W is thus found to be 5·05.

The results given in Table I. are represented by the curves in figs. 1 and 2, which give the values of W and k for different values of the ratio Z/p.

3. In Table II. are given the values of the mean velocity of agitation u of an electron, its mean free path l at 1 mm. pressure of gas, and the proportion λ of the energy of an electron which is lost in a collision with a molecule, these three quantities having been calculated from the above values of W and k by means of the formulæ

$$u = 1{\cdot}15\sqrt{k}\times 10^7 \text{ cm./sec.}$$

$$l = (7Wu/Z)\times 10^{-16} \text{ cm.}$$

$$\lambda = 2{\cdot}46\,W^2/u^2.$$

Table II.

	Neon containing 1 per cent. of helium.					Pure Neon.	
Z/p.	k.	$W\times10^{-5}$.	$u\times10^{-7}$.	$l\times10^2$.	$\lambda\times10^5$.	$l_n\times10^2$.	$\lambda_n\times10^5$.
·06	23·5	3·3	5·58	21·5	8·6	22·3	7·9
·1	34·5	3·95	6·75	18·7	8·4	19·3	7·8
·2	62·0	5·0	9·05	15·8	7·5	16·2	6·9
·3	89·0	5·72	10·85	14·5	6·85	14·8	6·3
·4	114	6·35	12·3	13·7	6·6	14·0	5·8
·5	137	7·05	13·5	13·3	6·7	13·5	5·8
·6	158	7·95	14·5	13·4	7·4	13·3	5·5
·8	194	9·65	16·0	13·5	9·0	13·7	6·9
1·2	235	15·0	17·6	15·4	17·9	15·6	...
2·0	275	27·0	19·1	18·0	49·0	18·3	...
4·0	308	53·0	20·2	18·7	170	19·0	...
6·0	316	74·5	20·4	17·7	330	18·0	...

* *Ibid.* p. 1039, fig. 3.

4. The proportion of helium present in the gas was determined by comparing the density of the latter with the known density of pure neon. The density of the gas was found by weighing it in a 250 c.c. flask and also weighing dry air (free from CO_2) in the same flask. It was found to be ·690 of the density of air, and since the corresponding ratio in the case of pure neon is known to be ·696, it follows that the gas contains 1 per cent. by volume of helium.

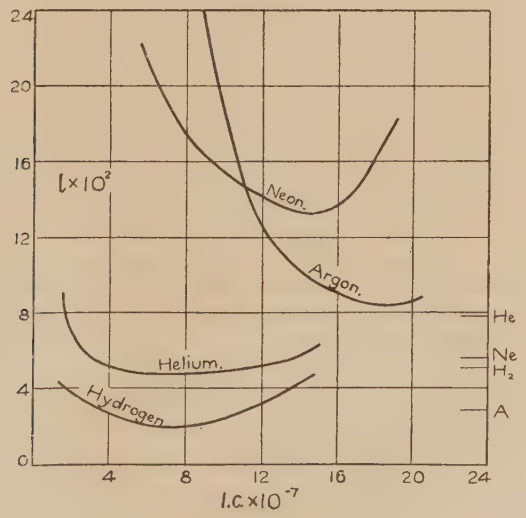
The values of l and λ for pure neon may now be calculated from those given in the fifth and sixth columns of Table II. by means of the formulæ

$$1/l = \cdot 01/l_h + \cdot 99/l_n,$$

$$\lambda/l = \cdot 01\,\lambda_h/l_h + \cdot 99\,\lambda_n/l_n,$$

where l_h, λ_h are the values of the free path and the fraction of energy lost for helium which were published recently *, and l_n, λ_n are the corresponding quantities for pure neon.

Fig. 3.



Values of l_n and λ_n calculated in this way are given in the last two columns of Table II., and those of l_n are represented by a curve in fig. 3. For purposes of comparison the curves for hydrogen, helium, and argon are also given in this figure.

* Phil. Mag. Oct. 1923.

It may be noticed from fig. 3 that for velocities u less than 10^8 the free paths are in the same order of magnitude as the atomic numbers. The lengths of the free paths deduced from viscosity measurements are indicated by short horizontal lines on the right border of fig. 3, and these are seen to be entirely different from the values deduced directly from the motion of the electrons. This emphasizes the dangers of the common practice of assuming values for the free paths of electrons which are deduced from measurements of viscosity, and also of assuming that they may be taken as independent of the velocity.

For each gas there is a range where l increases considerably as u diminishes, a property which has been shown to exist also for nitrogen, oxygen, carbon dioxide, carbon monoxide, and nitric oxide.

All four gases have minimum values of l, which correspond to velocities of about 1·4, 1·4, 5·7, and 9·6 volts for hydrogen, helium, neon, and argon respectively.

If it were assumed that the collision between an electron and an atom of an inert gas resembles that between two perfectly smooth and elastic spheres of masses m and M respectively, a simple calculation shows that the value of λ should be $2m/\mathrm{M}$. In the case of helium, neon, and argon this ratio has the values 27×10^{-5}, $5{\cdot}4 \times 10^{-5}$, and $2{\cdot}7 \times 10^{-5}$ respectively, which agree with the lowest of the experimental results as far as the order of the quantities is concerned. But this approximate agreement must not be taken as indicating that the collisions are to be treated as if the electrons collided with elastic spheres of fixed diameter, for the results show that with the smaller velocities there are many collisions in which the electrons are not appreciably deflected, and, if these collisions were taken into consideration in estimating the average fraction of energy lost in each collision, the values of λ obtained would be much smaller than the numbers given in this and in the previous papers to which I have referred.

This investigation has been carried out in Professor Townsend's laboratory, and I am also indebted to him in many other ways which assisted it to a successful termination.

XXXI. *The Mass-spectra of Chemical Elements.*—Part V. *Accelerated Anode Rays. By* F. W. Aston, *D.Sc., F.R.S., Fellow of Trinity College, Cambridge* *.

THE last communication of this series † contained a description of work carried out up to the end of 1922. It was there pointed out that the difficulties in the way of extending the method of mass-spectrum analysis to other elements lay not so much in the analysis as in the production of their mass-rays ‡. It was particularly desirable that a method should be evolved to give the mass-rays of the metallic elements which form so much the greater number of those not yet analysed. In this connexion it is of interest to note that, of all the ordinary non-radioactive non-metallic elements, only one, Tellurium, had failed to give a mass-spectrum.

Experiments with a Vacuum Arc.

The first essay in this direction was an attempt to draw out the ions formed in a vacuum arc between metallic points. The writer is indebted to Professor Merton for this suggestion, and also for advice as to possible means of carrying it out. An arrangement was made by which a heavy current could be automatically interrupted between a vibrating iron wire and the extreme edge of a stationary brass plate. The use of these metals insured the presence of at least three different types of ions all of reasonable mass. The device was simply a modification of the old Ruhmkorf interrupter, and the arcing was increased by introducing an inductance into the circuit. After a few trials it was found possible to maintain a strong discontinuous arc in a high vacuum for considerable periods. This arc was placed a few millimetres away from the pierced cathode of any ordinary parabola positive ray analyser, and its position carefully adjusted until it was exactly in line with the fine tube. The whole of the apparatus producing the arc was now maintained at a high potential of 20 to 30 kilovolts above that of the earthed cathode by means of a coil and rectifying valve. It was hoped that by this means some of the positive ions would be attracted out of the arc by the powerful electric field, and

* Communicated by the Author.

† Phil. Mag. xlv. p. 934.

‡ The term *"mass-rays"* has been suggested by Andrade ('The Structure of the Atom,' p. 83) to cover all swiftly moving particles of matter other than electrons. It therefore includes canalstrahlen, positive rays, anode rays, etc., each of which has a more limited meaning. The term seems admirably suited to its purpose, and in my opinion is a very welcome addition to the vocabulary of the subject.—F. W. A.

would form a stream of mass-rays directed down the fine tube of the analyser.

Many experiments were made, some with very prolonged exposures, but in no case was any trace of a parabola detected, and the method was reluctantly abandoned as impracticable. This is unfortunate, for had it succeeded it would doubtless have been as generally applicable as the arc in the optical spectra. The reason for so complete a failure is not obvious, but it is possible that though the abstracting field was of the order of 100 K.V. per cm., the local fields in the arc may have been even greater.

Experiments with Anode Rays.

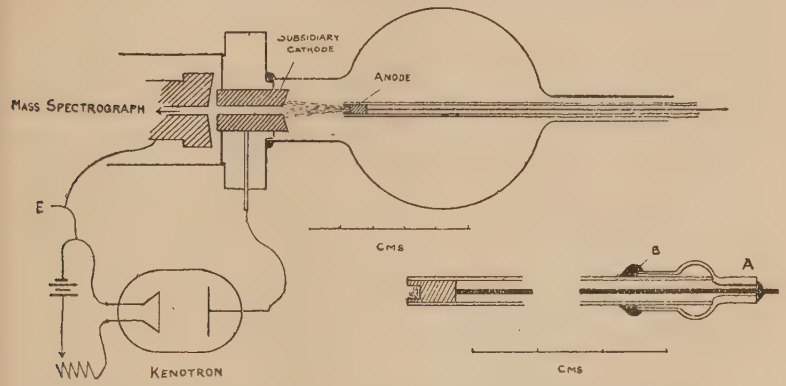
After this set back the only remaining hope appeared to lie in anode rays. Of the two methods for producing these rays, described in the pioneer work of Gehrcke and Reichenheim, one, the Hot Anode method, had already been applied to the mass-spectrograph, but, although by its means the composition of the alkali metals * had been ascertained, it gave little hope of wider development. The other, which made use of a Composite Anode composed of a mixture of graphite and metallic salts, gave more promise, as it had already been applied with success by G. P. Thomson to the parabola method of analysis in the case of the lighter elements of groups I. and II.† A preliminary set of experiments was therefore undertaken to find out the best method of obtaining an intense beam of rays in a given direction under conditions suitable for use with the mass-spectrograph.

It is not intended to describe these experiments in detail. Discharge-tubes of a great variety in size and shape were tried, and the electrodes placed in all sorts of positions. Hot tungsten subsidiary cathodes were used in some cases in the hope of lowering the working pressure but without success. The same parabola analysis apparatus which had previously given the lithium parabolas ‡ was employed in the tests. The same mixture of lithium, sodium, and potassium halides was used on the anodes, so that the relative efficiency of each type of apparatus could be quickly gauged by the visual brightness of the Li^7 parabola on the willemite screen. After a month of continuous work, a form of apparatus had been evolved which was capable of giving a strong visible lithium parabola continuously for several minutes. At this stage it was considered worth while applying the method to the mass-spectrograph.

* Phil. Mag. xlii. p. 436.
† Phil. Mag. xlii. p. 857.
‡ Phil. Mag. xlii. plate xv.

Apparatus for accelerated Anode Rays.

The general form of the apparatus with which the best results were obtained is shown diagrammatically in the accompanying rough scale drawing. The discharge-tube is comparatively small and shaped as illustrated. The construction of the anode is indicated in detail on a larger scale. The graphite paste is pressed into a hole drilled in the end of a small steel cylinder. This is carried on a long brass wire so that it can be slid into a pyrex glass tube, about 20 cm. long, fitting it closely. The working position of the steel container is with its face containing the paste flush with the end of the tube, which is cut off exactly at right angles. The thickness of the walls of the container is exaggerated in the sketch. It is actually made as small as possible consistent



with strength, so that the anode looked at end on from the cathode appears simply as a graphite disk surrounded by a glass ring. Since the working of the apparatus is extremely capricious and liable to be altered entirely in character by the slightest variation in the position of its parts, it was essential that the anode container could be withdrawn, refilled, and replaced with great exactness. It was so arranged that when the glass cap A was pushed as far as it would go on the tube the container would be exactly in position. Withdrawal and replacement could be made any reasonable number of times by melting the wax joint B. The pyrex glass tube was carried in the long narrow neck of the discharge-bulb, and so held in position. The best working position of the anode was as indicated. The discharge producing the anode rays took place between the graphite paste and subsidiary cathode. The latter was an aluminium cylinder pierced for the passage

of the rays and hollowed at its working surface to concentrate the cathode rays on the anode. It was mounted in a block of ebonite just in front the earthed cathode of the mass-spectrograph*.

During the preliminary experiments when the cathode of the discharge-tube itself was earthed, it was found, in the first place, that good beams of anode rays could only be obtained when the pressure in the discharge-tube was comparatively high and the potential consequently too low to be convenient for use with the mass-spectrograph. In the second place, the discharge itself was exceedingly unstable, for increase of current meant a hotter anode ; this led to the liberation of more gas, which caused further increase of current. On the other hand, if the anode was allowed to get too cold, the tube went hard and ceased to conduct altogether.

Both these difficulties were overcome by the introduction of a secondary cathode connected to earth through a kenotron as indicated. For if the earthed filament of the kenotron is maintained at a definite temperature—sufficient, for example, to give a saturation current of one milliampere—it is impossible to force more than one milliampere through it. Hence, whatever the conditions of the discharge-tube, short of absolute non-conductivity, the current through it will remain constant. It will be realized at once that this arrangement supplies exactly the stabilizing influence required. If the discharge-tube gets harder the potential drop between the anode and the subsidiary cathode will increase, hence the energy of the beam of cathode rays will increase ; this will raise the temperature of the anode and soften the tube. On the other hand, if the tube gets too soft the energy of the cathode-ray beam will decrease, cooling the anode and hardening up the tube again.

In addition, the main discharge can now be regulated to give rays of any required energy independent of the hardness or softness of the discharge-tube. If we put a mean of 24 watts through the secondary circuit at a current of 1 milliampere the anode will be maintained at a mean potential of 24 K.V. above earth, and the rays after leaving the subsidiary cathode will be *accelerated* to a velocity corresponding to that potential. Thus, if the potential between the anode and the subsidiary cathode is, say, 8 K.V., the accelerating potential will be 16 K.V. ; if the discharge potential falls to 6 K.V. the accelerating potential will automatically rise to 18 K.V., and so on.

* *Vide* Phil. Mag. xxxix. p. 613.

The kenotron with which the device was first tried was a high vacuum valve, made for an entirely different purpose, kindly lent by Dr. E. V. Appleton. For this experiment its grid and plate were connected together. This was later replaced by the simpler form of valve with no grid, shown in the sketch. These small kenotrons were kindly supplied by the M. O. Valve Co. The short straight filament only takes about 5 watts to heat and the kenotron behaves perfectly, working continuously for indefinite periods without any attention whatever.

Experimental Procedure.

The idea of the general working of the apparatus will be best conveyed by the description of a typical experiment performed after the conditions of the discharge-tube, position of the anode, etc., had already been shown satisfactory by preliminary photographs of the mass-lines of lithium. The first operation is the formation of the anode paste. The halide salt of the element to be studied is mixed with solid anhydrous lithium iodide and sometimes, in addition, other salts—such as lithium phosphate, potassium iodide, or sodium chloride—are added in small quantities. The mixture is pounded with about an equal weight of graphite powder—commercial stove polish, not graphite flakes—in a small agate mortar. After thorough incorporation the powder is moistened with a little saturated solution of lithium iodide, and the mixing and pounding continued very thoroughly with the resulting stiff paste.

Air is now admitted to the apparatus, the wax joint B melted, and the used container withdrawn and emptied. The freshly prepared paste is filled in and levelled to the rim. The container is now gently and cautiously heated over a bunsen flame to dry and consolidate the paste, the surface of which is smoothed from time to time. The heating is generally continued until iodine begins to come off in considerable quantity. The anode is then slid up to the end of the pyrex tube and the joint B remade.

Exhaustion is commenced as soon as the joint has set and its progress watched by passing a weak discharge with the kenotron short-circuited. At the same time the two charcoal tubes of the mass-spectrograph are heated. As the anode is heated up by the discharge water vapour is given off, shown by its typical violet discharge. After a time, generally a few minutes, the colour of the discharge changes abruptly to the dirty yellowish grey of iodine, the anode face glows with a brilliant red showing the lithium lines, and sometimes, but

not always, a bright divergent red beam of anode rays becomes visible. At this stage the discharge is stopped, the exhaustion continued with the Gaede pump to a very low point. Liquid air is applied to the charcoal tubes of the camera and slit system, the taps connecting these to the discharge-tube and pump are turned off, and the whole left for about half an hour to become completely exhausted.

The subsidiary cathode is now disconnected from earth and the kenotron put into action by heating the filament. The discharge is started by introducing a trace of gas, usually CO_2, into the discharge-tube. The anode immediately heats up and the pump is started at once to remove gas as it is evolved, for if the pressure is allowed to get too high sparking may take place between the subsidiary cathode and the earthed cathode, short-circuiting the kenotron and destroying its stabilizing effect. As the current through the primary of the main induction-coil and the heating current of the kenotron filament are both completely under control, the current passing through the discharge and the potential of the anode can be set at any required values. These were usually 1 to 1·5 milliampere and 24 to 30 K.V. When the appearance of the discharge is considered satisfactory the magnetic field of the mass-spectrograph is set, the plate exposed, and the exposure started by switching the electric field—usually 240 volts—on to the deflecting plates. The discharge cannot be stopped and started again like an ordinary gas discharge, for it and the heating of the anode are interdependent. If an accidental stoppage occurs the anode at once cools down and more gas must be introduced to start operations afresh. As the exposures are long the subsidiary cathode heats up considerably, and in order to prevent the melting of the wax joint surrounding it at the neck of the discharge-tube it is necessary to keep this under a continual air blast from a small fan.

It has not yet been found possible to obtain a beam of anode rays sufficiently strong for any mass-line to be visible on the willemite screen, as are the lines of hydrogen with the ordinary method. On this account the first three or four minutes of the discharge are generally utilized in recording the lithium lines as a necessary check on the working of the whole apparatus. The deflecting plates are then earthed, the photographic plate moved to a fresh position, and the magnetic field set for the element under investigation. The exposure is started as before by switching on the electric field, the discharge being maintained uninterrupted throughout these operations.

With all elements other than the alkali metals the effects are very faint, so the exposures are prolonged as far as possible until the anode drys up or it is judged that further continuation is useless. Most of the results, when the apparatus was working particularly well, were obtained with exposures of about half-an-hour, but in some cases the discharge was maintained for one hour and a half.

At the beginning of the discharge the anode surface is comparatively cool and glows brilliantly red, showing the lithium spectrum. The bright divergent beam of lithium anode rays never lasts many minutes of the exposure. Its appearance is a good sign, but equally bright lithium mass-lines have been obtained when it could not be seen at all. A valuable indication that the anode surface is functioning properly is the appearance of a small cloud of sodium light surrounding it, exactly as in the case of the Hot Anode experiments*.

As the gases come off less and less rapidly from the anode intermittent pumping only is required to keep the pressure down, and the latter and longer portion of the exposures is generally carried out without pumping at all. The anode by now has lost its lithium glow and becomes red and sometimes white hot. Lithium mass-rays are probably absent at these later stages, but the lines of the heavier members of the alkali group, if they are present in the anode paste, still continue to come off with the undiminished intensity, and in the case of other elements the high temperature of the anode surface seems favourable and may be essential. The general glow discharge, dirty yellow at the start, becomes blue-grey in the later stages.

Experimental Results.

The principal difficulty in the way of successful working of the method is complete ignorance of the mechanism of the discharge, which is probably very complex. It behaves at times in the most capricious and unaccountable manner. Each time the discharge-tube is altered or even taken down for cleaning entirely different results may be obtained. When by good fortune all is well the arrangement is capable of a surprisingly good performance. Thus, after a particularly favourable setting of the apparatus, six elements were successfully analysed in as many working days. On the other hand, when dismantling became imperative and it was cleaned and rebuilt—exactly as before, as far as one can tell,—no results of any value were obtained during weeks of work.

* Phil. Mag. xlii. p. 438.

Under these conditions any additional uncertainty in the procedure could not be tolerated, so schumannized plates, for which uniformity cannot be guaranteed, were only used when absolutely necessary. Normally the commercial half-tone plates were used, which are quite satisfactory for the detection of faint lines, as long as these are not too close to others. In their photographic intensities mass-lines obtained with anode rays cannot compare in any way with those obtained by the ordinary gaseous discharge, and are generally too faint for satisfactory reproduction. The pressure in the discharge-tube is relatively high, so that the vacuum in the slit system and camera is not so perfect. Also the exciting voltage found most suitable is not very high, and both these causes tend to render the lines obtained less sharp.

The method appears to be capable of very wide application to metallic elements. Those of Group I. are much the easiest to deal with and those of Group IV. apparently the hardest. The difficulty of obtaining the mass-rays appears to increase with increasing atomic weight, an effect which may be ascribed to decreasing velocity of the rays. The quantity of material necessary is only a few milligrams, of which much can be recovered after the experiment, so that it is particularly suitable in cases where only small quantities are available. High purity, as in other mass-spectrum measurements, is, in general, of quite subordinate importance.

In the matter of interpretation, the results of accelerated anode rays are very nearly ideal. The ordinary discharge-method gives altogether too many lines due to atoms and molecules other than those under consideration, the hot anode method gives too few, rendering measurement difficult. The new method gives pratically no molecular lines at all, and the atomic ones generally present are just about what is required for a satisfactory system of reference, and no more. The most important of these lines are C^{12}, Al^{27}, Si^{28}, Fe^{56}, I^{127}. It is not difficult to recognize possible sources for these lines, but it is a rather strange thing that iodine should always give a strong line, while those of the other halogens are seldom perceptible, even though they are present in the anode in much greater proportion.

Experiments with the Light Elements.

The first use to which the new method was put was to obtain accurate mass-measurements of the isotopic constituents of some light elements, the constitution of which had already been determined by other and rougher methods. It

was considered very probable that the masses of these might differ from whole numbers by a greater percentage than those of the heavier ones.

Lithium.—The lines of this element, as has already been stated, were used to test the working of the apparatus. In consequence, a very large number of mass-spectra were taken showing the lines 6 and 7. They were obtained under a great variety of discharge-conditions, but in no case was any variation in their relative intensity observed. This is very strong evidence that the variation in relative intensity observed by G. P. Thomson * and Dempster † must have been a spurious effect. The later work of Dempster on the relative intensities of the components of zinc suggests that in his case the error was an instrumental one ‡ Measurements of both the lithium lines were made on a number of plates where they could be compared with the carbon line, which was assumed to be 12 exactly. The eight best measurements of the heavier isotope gave a mean value $7{\cdot}006 \pm 0{\cdot}005$. The four best of the lighter gave $6{\cdot}008 \pm 0{\cdot}005$. The deviation is in the direction expected for a nuclear packing looser than that of helium, but it is in neither case much more than the error of experiment.

Beryllium.—G. P. Thomson § only obtained one parabola with this element, and decided that it was therefore simple with a mass-number 9, notwithstanding the fact that its chemical atomic weight was then taken as 9·1. His conclusion has been practically confirmed by the recent work of Hönigschmid, who gives the atomic weight as 9·018. In the present experiments an anode of beryllium fluoride mixed with a little lithium iodide and lithium phosphate was used. Long exposures were required to obtain the beryllium line strong enough for good measurements. Comparison with carbon ($C=12{\cdot}000$) on one plate and with lithium ($Li^7=7{\cdot}006$) on another gave values 9·003 and 9·001 respectively.

Magnesium.—The isotopes of this element have already been determined by Dempster, but since the arrangement of mass cannot with his method be carried out with accuracy it was of interest to check his results on the mass-spectrograph, particularly with regards to the whole-number rule. An anode mixture containing magnesium chloride was used, and with some difficulty the principal line of the elements, 24, was obtained and measured against Na^{23}. It showed no

* Phil. Mag. xlii. p. 861.
† Phys. Rev. xviii. p. 420.
‡ Phys. Rev. xx. p. 636.
§ *Loc. cit.*

measurable deviation from the whole-number rule; the effects were too faint for the lines of the two other constituents 25 and 26 to be seen.

Calcium.—This element, like magnesium, does not produce anode rays at all readily. Several experiments were made with it. In some the fluoride was used, in others the chloride, but in no case was the Ca^{40} line as strong as that of K^{39}, although potassium was carefully excluded from the anode mixture. The alkali metals are abnormally sensitive to this method, and it is possible that its source was the pyrex-glass. The weakness of the principal calcium-line precluded any possibility of detecting its exceedingly faint companion at 44, discovered by Dempster, but on the best of the spectra obtained the expected second-order line at 20, searched for without success by G. P. Thomson *, was distinctly visible. The first and second order lines of calcium, both lines of potassium, and the strong single lines of sodium and aluminium could all be compared on the same spectrum, and were found integrally related to each other within the error of measurement. We are therefore faced with the remarkable conclusion that the two isobaric atoms Ar^{40} and Ca^{40} probably do not differ in weight by one tenth per cent., although the structure of their respective nuclei *must* be different, for one contains two more electrons than the other.

Germanium (At. Wt. 72·38).

To investigate this element the fluoride was used. It was made from a sample of pure oxide kindly supplied by Professor L. M. Dennis of Cornell University. The oxide was simply heated with strong hydrofluoric acid and evaporated to dryness. The exact chemical constitution of the resulting material is of little importance, it appeared stable at high temperatures, and when incorporated with alkaline halides worked very well.

The mass-spectrum of germanium consists of three lines—70, 72, and 74, of intensities very roughly estimated as proportional to 2 : 4 : 5. No variation from the whole-number rule was observed, so that these intensities agree fairly well with the chemical atomic weight. It will be noticed that Ge^{70} is isobaric with the weakest and heaviest component of zinc discovered by Dempster, and that Ge^{74} is isobaric with the very weak lightest isotope of selenium.

* *Loc. cit.* p. 862.

Copper (At. Wt. 63·57).

For this element an anode of cuprous chloride, lithium iodide, and rubidium chloride was used. The last salt was added to provide reference-lines. The effects obtained from copper were faint, but very conclusive, as both in intensity and position its lines appeared exactly as statistical considerations had led one to expect. These lines are 63 and 65; they were measured against Rb^{85} on one side and Fe^{56} on the other, and show no measurable deviation from the whole-number rule. The ratio of their intensities was about 2·5 : 1, in good agreement with the chemical atomic weight *.

Strontium (At. Wt. 87·63).

Many experiments were done with this element. Its chloride, bromide, and iodide were all tried. The last seems to work the best, and was used mixed with lithium iodide and a little lithium phosphate. Strontium gives a remarkably bright visible beam of anode rays which usually persists long after the red lithium beam has disappeared. Its mass-spectrum shows a single line at 88. This line is always accompanied by rather more penumbra than usual, but it has all the characteristics of a true single line. The chemical atomic weight suggests the presence of at least one lighter constituent, so the experiments were repeated with schumannized plates. On these the penumbra was greatly reduced, so that a close component of any reasonable intensity must have been detected. None was observed, and the mass-measurements, relative to the iodide line, though not quite so accurate as usual, make it impossible to suppose that the divergence from a whole number could be sufficient to account for the fractional atomic weight. It is therefore difficult to escape the conclusion that the accepted figure given above is too low.

Cobalt (At. Wt. 58·97).

Anhydrous cobaltous chloride was employed and mixed with sodium chloride and the usual lithium salts. A trace of rubidium present gave a valuable reference-line. Cobalt is a simple element characterized by a line at 59, exactly as was expected from its atomic weight, taken in connexion with the

* In 'Nature,' July 7th, Dempster described some results obtained with his apparatus, which led him to the conclusion that copper had three isotopes all of even atomic weight. The relative intensities of these lines suggested that they were probably due not to copper but to zinc adventitiously present (*vide* 'Nature,' Aug. 4th). He has since accepted this as the most probable explanation.—F. W. A.

empirical rule connecting odd atomic number with odd atomic weight. Measurements of the line were made with reference to Fe^{56} and Rb^{85}, and showed no deviation from the whole-number rule.

Scandium (At. Wt. 45·10)

The only source of this rare element which happened to be available was a sample of the pure aceto-acetate kindly supplied by Professor G. Urbain of Paris. A small quantity of this was boiled with nitric acid and then ignited. The resulting powder was then treated with hydrofluoric acid, evaporated to dryness, and mixed with potassium iodide and lithium iodide for treatment. On the mass-spectrum only one new line at 45 could be distinguished, which when compared with K^{39} appeared accurately integral. Although long exposures were given, this line was always faint, so that the presence of small quantities of another constituent, expected at 47, could not in any case have been detected. Scandium may, therefore, be regarded as consisting mainly of atoms of mass-number 45, but further work will be necessary to prove the presence or absence of a second isotope suggested by the fractional atomic weight.

Manganese (At. Wt. 54·93).

Manganese fluoride made by the action of hydrofluoric acid on the pure carbonate was used mixed with lithium iodide. The appearance of these bodies when they were mixed suggested that a reaction of some sort took place. The mixture worked unusually well as an anode, and during the first few minutes of the discharge gave a good visible beam of anode rays. Contrary to all expectations, the beam was yellow and showed the sodium line only without a trace of the usual ones of lithium. No reason can be given for this phenomenon, which is characteristic of the frequent capricious and unaccountable behaviour of the discharge. Manganese is characterized by one line of mass-number 55, as expected from its atomic weight. It was measured against the neighbouring line of iron and showed no measurable divergence from an integer.

The mass-number of manganese has one particular point of interest. It is the eighth term of the well-known recurring series 2, 3, 5, 8, 13, . . . All the preceding terms correspond to gaps in the list of mass-numbers known to exist*.

* 'Isotopes,' p. 111.

Gallium (At. Wt. 69·72).

Abortive attempts to obtain the mass-spectrum of this element by means of its volatile chloride have already been described. It was successfully attacked by means of the new method by the use of its fluoride made by the action of hydrofluoric acid on a very pure specimen of the hydrate, for which the writer is indebted to Professor T. W. Richards of Harvard. The results obtained were faint, but gave satisfactory proof that the element consists of two components of mass-numbers 69 and 71. The intensity relation between the two lines agrees much better with Richard's recent determination of the atomic weight quoted above than with the value 70·1 previously in use.

Vanadium (At. Wt. 50·96).

An anode consisting of vanadium chloride mixed with a little lithium iodide gave satisfactory results. A single line appeared at the expected position corresponding to mass-number 51. This was compared with K^{39} on the one side and with Fe^{56} on the other, and showed no measurable variation from a whole number.

Chromium (At. Wt. 52·01).

The first experiments with this element were unsuccessful, but a second attempt during the period already alluded to when the experimental conditions were abnormally good succeeded at once. An anode containing chromium chloride, commercial chromium fluoride, and the usual lithium salts was used. The discharge after a few minutes became a rather unusual violet in colour and the anode was at a bright red heat throughout the entire exposure of 35 minutes. The single chromium line at the expected mass-number 52 was rather faint but unmistakable. Its integral value was established by comparison with Fe^{56}.

Titanium (At. Wt. 48·1).

The production and identification of the mass-rays of this element present quite peculiar difficulties. The failure of experiments on its volatile chloride by the ordinary discharge-method has already been described in these reports. It belongs to a chemical group which appears to be the least favourable to the production of anode rays. In the first attempts made with the new method potassium titanifluoride was employed. On the mass-spectra produced faint indications of a line at 48 could be seen, but were valueless for

the following reason. A fairly strong line appeared at 47. This was undoubtedly due to $Si^{28}F$, so that part if not all the effect at 48 could be ascribed to $Si^{29}F$. A later experiment in which the fluoride made by the action of hydrofluoric acid on the pure oxide was more successful. This gave a line at 48 not only reasonably strong but much stronger than that at 47, now feeble, so that there is little doubt that the principal constituent of titanium has a mass-number 48. On one spectrum a very faint ghost could be distinguished at 50. If this should prove to be a true isotope, it would tend to support Hönigschmid's value of the atomic weight given above, rather than the lower value 47·88 more recently suggested by Baxter.

Silver (At. Wt. 107·88).

An anode containing silver chloride and lithium chloride, though behaving rather unsteadily as regards discharge, gave a very definite result. Silver has two isotopes, whose mass-lines when measured against that of iodine have integral values 107 and 109. The first of these is slightly the brighter. Owing to the weight of accumulated statistical evidence in connexion with the relation between odd atomic number and odd atomic weight, and the exceptional trustworthiness of the chemical atomic weight work on silver, this result might be described as a foregone conclusion.

Yttrium (At. Wt. 88·9).

A small quantity of this rare element in a state of metallic powder was dissolved in hydrofluoric acid. The resulting fluoride worked quite well when mixed with lithium iodide. The mass-spectrum showed one line only, which, when compared with I^{127}, gave a value 89 integral within experimental error. It will be noticed that this number is the ninth term in the series mentioned under manganese. The success of the method in generating the mass-rays of scandium and yttrium holds forth hopes of its applicability to all the rare earth elements.

Experiments with Zirconium and Hafnium.

The new element hafnium presents a unique opportunity of determining the atomic weight by the mass-spectograph before any satisfactory value has been obtained by chemical means. Unfortunately, the titanium, zirconium, hafnium group appears the most difficult to tackle of all, so far as production of mass-rays is concerned. The first experiments on zirconium were done with a fluoride made by dissolving in hydrofluoric acid a small quantity of a rich mineral zircon,

kindly supplied by Dr. Dootson. Even with the longest exposures no reliable indication of the zirconium lines could be seen, though on one plate a doubtful trace could be distinguished at 90, which may have been due to the main constituent of the element. It was already realized that increase of atomic weight decreases the chance of getting mass-lines, so that this result extinguished all reasonable hope for the much heavier element hafnium. As, however, Dr. Hevesy had been kind enough to supply a sample of potassium hafni-fluoride, estimated to contain about 50 per cent. zirconifluoride, a careful trial was made with this material. As had been feared, no lines in the region 178 could be seen at all, though again there was the suggestion of a line at 90, possibly zirconium. It is hardly necessary to state that this failure does not suggest in the slightest degree that hafnium was not present. It only indicates a conclusion, which further experiments with pure zirconium fluoride have confirmed, that it will be exceedingly difficult to obtain satisfactory mass-spectra of these elements.

Other Experiments yielding Negative or Inconclusive Results.

Experiments with niobium, molybdenum, cadmium, and lead have so far given no indication whatever of the mass-lines of these elements. The results with barium were not entirely negative, since a slight effect was visible on the plate in the expected position. This suggested that barium has several isotopes, and there is little doubt that its composition could be determined if a sufficiently advantageous setting of the discharge-tube could be made. Attempts to get the principal line of iron 56 so strong that the presence or absence of the possible weak component 54 could be established have so far been unsuccessful.

Table of Results.

Element.	Atomic Number.	Atomic Weight.	Minimum Number of Isotopes.	Mass-numbers in Order of Intensity.
Sc	21	45·1	1	45
Ti	22	48·1	1	48
V	23	51·0	1	51
Cr	24	52·0	1	52
Mn ...	25	54·93	1	55
Co	27	58·97	1	59
Cu	29	63 57	2	63, 65
Ga.....	31	69·72	2	69, 71
Ge.....	32	72·5	3	74, 72, 70
Sr	38	87·63	1	88
Y	39	88·9	1	89
Ag.....	47	107·88	2	107, 109

If one adds these results to the table given in the previous report of this series * it will be seen that the first thirty-nine elements in sequence have been analysed and, in addition, seven more of higher atomic number, so that the constitution of rather more than half the known elements has been established, in most cases with considerable certainty. The new results given in this paper strengthen the empirical laws observed to hold relating to the connexion between atomic number and atomic weight. In the case of the elements of odd atomic number, the rule that they cannot have more than two isotopes still shows no exception, and the law that their atoms should have odd atomic weight is satisfied by all the elements in the list given above. The only exceptions to the latter law, which means that the nuclear electrons are always associated together in pairs, are nitrogen and the two weaker isotopes of lithium and boron, all very light elements. In a curiously large number of cases a difference of atomic weight 44 is connected with a difference of atomic number 18, and gives a pair of elements having similar chemical properties, as the following list indicates :—

Mg 24 Mg 26 Al 27 Si 28 Si 30? P 31 S 32 Cl 35 Cl 37 Ar 36 Ar 40
Zn 68 Zn 70 Ga 71 Ge 72 Ge 74 As 75 Se 76 Br 79 Br 81 Kr 80 Kr 84

Ca 44 Sc 45 Cu 63 Cu 65.
Sr 88 Y 89 Ag 107 Ag 109.

In conclusion, the writer wishes to thank Sir William Pope for placing at his disposal for this work a great variety of metallic compounds, and to Mr. Stokeley for his valuable personal assistance in this connexion. He also wishes to repeat his acknowledgment to the Government Grant Committee of the Royal Society for part of the apparatus employed in this research.

Summary.

A new method of producing anode rays suitable for mass-spectrum analysis is fully described, together with experiments which led to its development.

By its means the principal isotopes of lithium, beryllium, magnesium, and calcium are shown to have atomic weights closely approximating whole numbers.

Experiments are described by which the constitution of twelve more metallic elements has been determined and a list of these and their isotopes is given.

Cavendish Laboratory, Cambridge,
November 1923.

* Phil. Mag. xlv. p. 944.

XXXII. *Ionization by Collision in Helium.* *By* J. S. Townsend, *M.A., Wykeham Professor of Physics, Oxford, and* T. L. R. Ayres, *M.Sc., D.Phil., Exeter College, Oxford* *.

1. THE experiments with helium which are described in this paper were made in order to determine the conditions under which the gas is ionized when electrons collide with molecules. They also provide a means of testing some of the various views of physicists on effects which may be produced when electrons with certain critical velocities collide with molecules of the gas.

We have been unable to reconcile the results of the experiments with the recent theories, and we find that the original theory of ionization by collision which was given many years ago affords a satisfactory explanation of the experiments. This theory was found by Gill and Pidduck † to be in good agreement with their experiments on the currents through monatomic gases obtained when electrons are set free from the negative electrode and move through various distances to the positive electrode under a uniform electric force.

It has been considered desirable to repeat these experiments with helium, and to extend the investigations in order to find the conditions under which the first set of additional electrons are generated by the electrons set free from the negative electrode. The results thus obtained provide a means of calculating the average velocities of electrons before and after the collisions with the molecules which are ionized. The method of finding these velocities and the energy required to ionize a molecule has already been explained in a paper recently published in the 'Philosophical Magazine' ‡.

The method was there applied to the results of a set of experiments in which the ratio of the electric force X to the gas-pressure p was 16, X being in volts per centimetre and p in millimetres of mercury, and it was found that the amount of energy required to ionize a molecule of helium was less than the energy acquired by an electron in moving between two points differing in potential by 14 volts. A large number of additional experiments have recently been made,

* Communicated by the Authors.

† E. W. B. Gill and F. B. Pidduck, Phil. Mag. (6) vol. xvi. p. 280 (1908), and vol. xxiii. p. 837 (1912).

‡ J. S. Townsend, Phil. Mag. vol. xlv. p. 1071 (May 1923).

taking various values of the ratio X/p, which are also in good agreement with the theory and confirm the result previously obtained as to the comparatively low value of the energy required to ionize a molecule of helium.

2. In order to find the velocities of electrons before and after the collisions in which molecules are ionized, it is necessary to examine certain stages of the development of the currents obtained between parallel plates when ultra-violet light acts on the negative electrode, and the distance x between the electrodes is varied while the electric force X and the gas-pressure p are constant.

A complete investigation may be considered to extend over three distinct stages. In the first stage, as the distance x between the plates is increased from zero up to a certain limit $x=a$, the mean energy of the electrons varies with the distance between the plates, and does not attain a final steady value until a considerable number of new electrons have been obtained by increasing x. In this stage it is convenient to represent the current in terms of the distance x or the potential difference Xx between the plates by a curve, as there is no simple formula representing the relation between the current and the potential.

In the second stage, from the distance $x=a$ to the distance $x=b$ the current is represented in terms of the distance x by the formula $n=n_0\epsilon^{\alpha x}$, which shows that the mean energy of the electrons and the distribution of the energies about the mean are the same in passing any plane parallel to the electrodes.

In the third stage, from the distance b up to the sparking distance the rate of increase of the current with the distance is greater than the increase of n as given by the above formula, and the current is given in terms of x by an equation of the form

$$n=n_0\frac{(\alpha-\beta)\epsilon^{(\alpha-\beta)x}}{\alpha-\beta\epsilon^{(\alpha-\beta)x}}.$$

For the purpose of this investigation it is not necessary to find the currents for distances between the electrodes greater than b, or to determine the process of ionization which causes the rate of increase of the current with the distance to exceed the rate given by the formula $n=n_0\epsilon^{\alpha x}$. It may be stated that there are no definite values to be given to distances a and b, as the mode of development of the current changes gradually as the distance x is increased.

3. In the experiments that have been made with helium

every precaution has been taken to have the gas free from impurities. The apparatus containing the adjustable parallel plates was constructed with glass insulation throughout, as it was found that ebonite surfaces may introduce impurities which have an appreciable effect on the motion of electrons. The apparatus was perfectly air-tight, and when exhausted to 1/100 of a millimetre pressure, it was impossible to detect any leak in the course of several days by means of a McLeod gauge. The method adopted to avoid mercury vapour was the same as that used in the experiments on the motion of electrons in helium which have recently been published *. As in the latter experiments, two specimens of helium were used, one obtained from a natural source and the other obtained by heating thorianite, and it was found that the effects due to ionization by collision were the same in the two specimens.

The plate electrodes were silver disks 6 cm. in diameter, the upper plate being carried by a micrometer screw in order that it might be set at any distance from the lower plate from 1 to 10 millimetres. The ultra-violet light from an external spark-gap passed through a quartz window in the base of the instrument and through narrow slits in the centre of the lower electrode, and fell normally on the upper plate which was the negative electrode. The slits in the lower electrode were about a centimetre long, a fifth of a millimetre wide, and 1 millimetre apart.

4. When the electric force X and gas-pressure p are constant, the currents i obtained with different distances x between the plates may be expressed by means of a curve in terms of the potential difference V between the electrodes. This curve remains unaltered when X and p are altered in the same proportion, but there is a different curve for each value of the ratio X/p. This result follows from the theory, and it has also been verified experimentally.

In any of these curves the ratio i_1/i_2 of the two currents corresponding to two given potentials V_1 and V_2 is independent of the number of electrons set free initially from the negative plate by the ultra-violet light. This result has been verified by changing the intensity of the light. All conclusions to be drawn from these curves must satisfy these conditions.

The currents were measured by an induction balance by a zero method, using a sensitive electrometer to indicate the

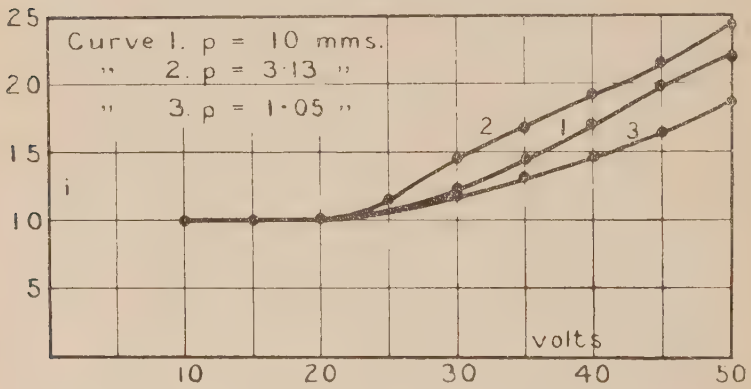
* J. S. Townsend and V. A. Bailey, Phil. Mag. vol. xlvi. p. 657 (Oct. 1923).

zero potential. They were all small currents of the order from 10^{-12} to 3×10^{-11} ampere.

Although these simple facts, which have been verified by experiments of this type, have been mentioned in the account given of previous researches, we think it necessary to repeat them, as they have been lost sight of in some of the theories that have been suggested to explain ionization by collision.

5. Several curves have been determined which give the relation of the current to the potential difference between the plates for different values of the ratio X/p. Three examples of these curves are shown in fig. 1, the ordi-

Fig. 1.



nates being proportional to the currents and the abscissæ proportional to the potential difference V between the plates or to the distance x between the plates, V being equal to Xx.

The same electric force X, 50 volts per centimetre, was used in determining the points on the curves. The distance between the plates was varied from 2 to 10 millimetres, so that the potentials of the positive plate were from 10 to 50 volts, the negative electrode being taken as the zero of potential. The first curve gives the currents in helium at 10 millimetres pressure, the second curve at 3·1 millimetres pressure, and the third curve at 1·05 millimetres pressure. Thus the values of the ratio X/p to which the curves correspond are 5, 16, and 47·5 respectively.

The ordinate 10 is taken to represent the current in each case when the plates are 2 millimetres apart. For each pressure the current was the same for the distances 2, 3, and 4 millimetres between the electrodes, so that the three curves coincide and are parallel to the x axis for the range of potentials from 10 to 20 volts, the currents consisting of the

electrons set free from the negative electrode by the ultra-violet light.

These electrons start from the negative electrode with a small velocity, and do not acquire sufficient energy to ionize the molecules of gas in appreciable numbers until after they have passed the plane where the potential is 20 volts. After passing this plane there is a continuous increase in the current, the rate of increase depending on the pressure of the gas.

If N be the number of electrons coming from the negative electrode, the number in the stream is $1{\cdot}5 \times N$ as it passes the 36-volt plane, and the number is 2 N as the stream passes the 45-volt plane when the pressure of the gas is 10 millimetres.

When the gas-pressure is reduced to 3·13 millimetres, the number of electrons in the stream is 1·5 N in passing the plane at 31·5 volts, and the number is 2 N in passing the plane at 42 volts.

When the gas-pressure is further reduced to 1·05 millimetres, the rate of increase of the current with the distance between the plates is diminished, the number of electrons in the stream being 1·5 N in passing the plane at 41·3 volts and 2 N in passing the plane at 53·5 volts.

6. In explaining the curves in fig. 1, it is of interest to know approximately the number of collisions each electron makes with molecules of the gas in traversing a given distance in the direction of the electric force. The mean free path of an electron in helium at 3·13 millimetres pressure is about $1{\cdot}7 \times 10^{-2}$ centimetre. It is unnecessary to take into consideration the variation of the mean free path with the velocity, as we are concerned only with the order of this length. In traversing 1 millimetre in the direction of the electric force, the electron does not move in a straight path for this distance, as its direction of motion is changed in each collision. The total length of all the free paths of an electron exceeds the distance it travels in the direction of the electric force in the same proportion as the velocity of agitation exceeds the velocity in the direction of the electric force. Thus the total distance that an electron travels through the gas while it moves 1 millimetre in the direction of the electric force is more than 4 centimetres *.

* The mean free paths and velocities of electrons involved in this calculation are taken from the paper on "The Motion of Electrons in Helium" which has just been published (J. S. Townsend and V. A. Bailey, Phil. Mag. Oct. 1923). The determinations refer to a range of values of the ratio X/p lower than the range which includes the cases where ionization by collision produces large effects, so that the estimate of the number of collisions given above is only an approximate estimate for these ranges of forces and pressures.

Hence, in the above experiments at 3·13 millimetres pressure, an electron collides with more than 100 molecules of the gas in moving 1 millimetre in the direction of the electric force. Although an electron may lose only a small proportion of its energy in a collision with a molecule that is not ionized, there is a very large number of such collisions, and the total loss of energy due to this cause is quite appreciable. Since there are more collisions at the higher pressures than at the lower pressures, the effect of this loss of energy is greater at 10 millimetres than at 3·13 millimetres. The reduction in the rate of increase in the current with the distance between the electrodes, when the pressure is increased from 3·13 to 10 millimetres, is obviously due to this cause.

The reduction in the rate of increase in the current, when the pressure is reduced from 3·13 to 1·05 millimetres, must be attributed to another effect. In passing through a plane at any fixed distance from the negative electrode, the energy of the electrons is greater at the lower pressure than at the higher pressures, since there is less loss of energy in collisions in traversing the space between the negative electrode and the plane. Thus, when the electric force is constant, the energy of the electrons in the collisions with the molecules which are ionized increases as the pressure is reduced.

When the pressure is below the value corresponding to $X/p=16$, the number of molecules ionized per millimetre diminishes with the pressure. This shows that ionization by collision only occurs in a small fraction of the total number of collisions of an electron with molecules, even when the energy of the electron in each collision is sufficiently large to ionize a molecule. The rate of increase of the current with the distance between the electrodes is therefore reduced when the pressure is reduced from 3·13 to 1·05 millimetres, because the total number of collisions is reduced, and consequently the probability of ionization by collision is also reduced.

7. Let c be the energy required to ionize a molecule, $(c+v)$ the energy of an electron before a collision in which a molecule is ionized. The quantity c may be taken as constant, but v varies over a wide range. Let $\bar{v}$ be the mean value of v for all the collisions in which molecules are ionized.

Let W be the loss of energy of an electron in the collisions with molecules which are not ionized in moving from the

negative electrode to the distance where it ionizes a molecule. The values of W vary over a wide range, since the values of δ and the number of collisions per centimetre is different for each electron. Let $\bar{W}$ be the mean value of W for all the electrons set free from the negative electrode.

If all the energies be expressed in volts, the energy of the electron when it is set free from the negative electrode is of the order of one volt, and it may be neglected in comparison with the principal quantities of energy which are being considered.

The electron acquires the energy $c+v$ in moving under the action of the electric force X through the distance δ, and it loses the amount W before arriving at the point where it ionizes a molecule. The following relation is obtained between the energies:

$$X\delta = c + v + W.$$

The curve 2 (fig. 1) giving the currents in helium at 3·13 millimetres pressure with the force of 50 volts per centimetre shows that a few of the electrons from the negative electrode ionize molecules before reaching the plane δ_1 where the potential $X\delta_1$ is 21 volts, while others do not ionize molecules until the plane δ_2 is reached, where $X\delta_2$ is 42 volts, this being the plane at which the number of electrons in the stream is 2 N. Thus there is a wide divergence between the values of $v+W$ for the different electrons which indicates that the sum $\bar{v}+\bar{W}$ is also large.

The quantities $\bar{v}$ and $\bar{W}$ are functions of the ratio X/p, and the values of $c+\bar{v}+\bar{W}$ corresponding to different values of X/p may be obtained from the areas of the curves (fig. 1.) Thus

$$c+\bar{v}+\bar{W} = \frac{1}{N}\int_N^{2N} V\, di = X\bar{\delta}. \quad . \quad . \quad . \quad . \quad (1)$$

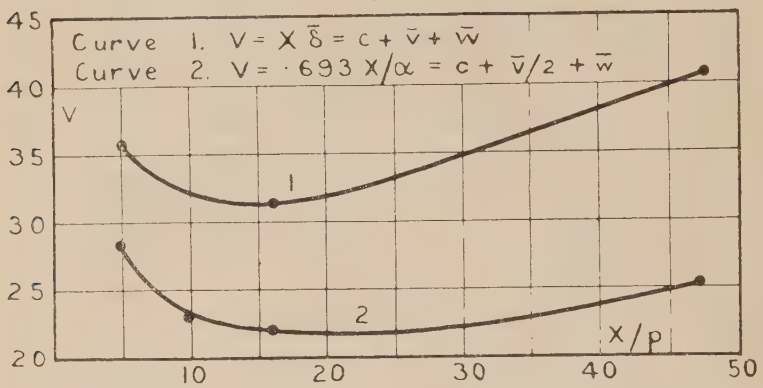
The mean potential $X\bar{\delta}$ is nearly the same as the potential at the point where the current is 1·5 N.

These potentials are represented by curve 1 (fig. 2) in terms of the ratio X/p, one point on this curve being obtained from each curve of the type shown in fig. 1.

8. The currents in the second stage of the process of ionization where the average velocity of the electrons is constant were determined with the same apparatus, using larger electric forces and gas-pressures. In this stage the

current is given in terms of the distance x between the plates by the formula $n = n_0 e^{\alpha x}$, and the value of α corresponding to any force and pressure is easily determined.

Fig. 2.



In these experiments the potential difference between the plates was generally less than 100 volts, so that no correction had to be made for effects due to other processes of ionization.

There is a considerable range of distances between the electrodes over which the currents in helium have been found to agree accurately with the above formula, and this result affords the principal reason for attributing the increase of current to the ionization of the molecules by the collisions of the electrons. If any other process contributed appreciably to the increase of current, there would be a large deviation from the formula. Within this range of distances between the electrodes the quantity α can be easily measured, and there is no appreciable error introduced by any other ionizing effect.

As it is necessary to be quite certain on this point, another investigation is being made in the laboratory to find by a more direct experimental method if there are other processes of ionization comparable with the direct effect of the collisions of electrons with molecules, when the ranges of potentials and pressures are the same as those used in the experiments on the determination of α. A full account of the investigation will be given in another paper, but it may be stated that the method was sufficiently sensitive to detect effects which might be due to ionization of molecules by the collisions with positive ions, or to electrons set free from the negative

electrode, either by impacts of positive ions or by radiation from molecules of the gas, but no effects due to these causes were observed under conditions where the currents were proportional to $e^{\alpha x}$.

The original theory of ionization by collision implies that ionization is due to one collision of an electron with an ordinary molecule, and that a certain relation must hold between the values of α, X, and p, which is expressed by the formula $\alpha/p = f(X/p)$. This relation has been tested with helium, and in the experiments where the ratio of the force to the pressure was constant the ratio α/p was also constant. If any appreciable effect arose from an impurity in the gas, this relation could only be obtained if the amount of the impurity were proportional to the pressure of the helium. The results of the experiments with different forces and pressures therefore show that it would be unreasonable to suppose that there is any appreciable error due to impurities, as it is extremely improbable that the amount of an impurity would increase with the pressure of the helium.

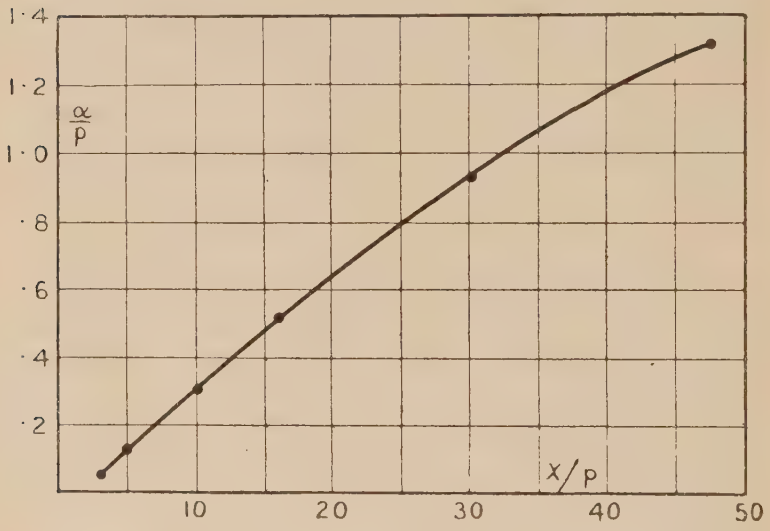
Also the factor $e^{\alpha x}$ is independent of the number of electrons in the current, as it was found that all the currents were changed in the same proportion when a large change was made in the number of electrons set free from the negative electrode by altering the intensity of the ultra-violet light.

If the ionization by collision in these experiments were due to two collisions of electrons with the same molecule, the number of electrons generated by collision would be proportional to the square of the current; but no change was observed in the values of α when the intensity of the current was changed in the proportion of 3 : 1, so that the experiments show quite conclusively that in each case where an electron is generated the molecule is ionized by a single collision.

9. The results of the experiments on the determination of α for helium may be represented in the usual manner by a curve giving the ratio of α/p in terms of X/p. The curve is given in fig. 3, and it shows that, if X be constant and p variable, α has a maximum value at the pressure for which the ratio X/p is the abscissa of the point of contact of the tangent from the origin, which is near the point $X/p = 16$. If X be 50 volts per centimetre, the maximum value of α is obtained when p is about 3·13 millimetres, α being 1·56. At the pressure 10 millimetres, $X/p = 5$ and $\alpha = 1{\cdot}22$; and at the pressure 10·5 millimetres, $X/p = 47{\cdot}5$ and $\alpha = 1{\cdot}37$.

These changes in the value of α are due to the same causes as the changes in the value of $X\bar{\delta}$. With the largest pressure the number of molecules ionized per centimetre is small, owing to the loss of energy of the electrons in the collisions with other molecules. With the smallest pressure although the average kinetic energy of the electron is increased, the number of molecules ionized per centimetre is reduced, owing to the reduction in the total number of collisions with molecules.

Fig. 3.



10. The currents in this stage are given by the formula $n=n_0e^{\alpha x}$; and if n_1 and n_2 be the numbers of electrons passing two planes at the distances x_1 and x_2 from the negative electrode, $n_2=2n_1$ when $e^{\alpha(x_2-x_1)}=2$. In this case the distance between the planes $(x_2-x_1)=\cdot693/\alpha$.

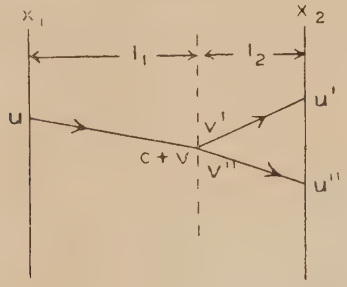
When an electron moving with the energy $c+v$ ionizes a molecule, the quantity of energy c is lost in separating the new electron from the molecule, and the remainder of the energy v is either retained by the original electron or divided between the two electrons. The mean energy of these two after the collision is therefore $v/2$.

In this stage the average value of $(c+v)$ for all the collisions in which molecules are ionized is the same as the average $c+v$ in the first stage, when the ratio X/p is the same in the two stages, provided $\bar{v}/2$ is not large compared with c

(or about 10 volts). Since the average energy of the electrons after collisions in which molecules are ionized is $v/2$, there is a wide divergence between the energies of the electrons in the stream, but the mean energy of the electrons passing any plane is constant. In the case of the two planes x_1 and x_2 where the numbers of electrons are n_1 and $2n_1$, the increase in the current with the distance is the same as if each electron passing the plane x_1 with energy u ionized one molecule in the space between the two planes and the mean energy of the two electrons as they pass through the plane x_2 is equal to u.

The average effect is represented by the diagram (fig. 4).

Fig. 4.



If an electron enters the space through the plane x_1 with energy u, its energy is increased to $(c+v)$ in moving the distance l_1 in the direction of the electric force X to the point where a molecule is ionized. The energy before the collision is given by the equation

$$c+v=Xl_1+u-w_1, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

w_1 being the energy lost by the electron in collisions with molecules which are not ionized while traversing the distance l_1.

If v' and v'' be the energies of the two electrons after the ionizing collision, $(v'+v'')$ is equal to v, and after moving the distance l_2 where $l_1+l_2=x_2-x_1$, their mean energy is equal to u. Let u' and u'' be the energies of the two electrons as they pass the plane x_2, then

$$\left.\begin{aligned} u' &= Xl_2+v'-w_2' \\ \text{and} \quad u'' &= Xl_2+v''-w_2'' \end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad (3)$$

w_2' and w_2'' being the loss of energy of the two electrons respectively in collisions with molecules which are not ionized while they traverse the distance l_2.

The mean energy which is equal to u is

$$\frac{u'+u''}{2} = \mathrm{X}l_2 + \frac{v}{2} - w_2,$$

where $w_2 = (w_2' + w_2'')/2$.

Thus $$c + v = \mathrm{X}(l_1 + l_2) + v/2 - (w_1 + w_2).$$

Since $l_1 + l_2 = x_2 - x_1 = \cdot 693/\alpha$, the following relation between the energies is obtained:

$$\frac{\mathrm{X}}{\alpha} \times \cdot 693 = c + \frac{v}{2} + w, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

w being the mean loss of energy of an electron in traversing the distance $x_2 - x_1$. The distance $\cdot 693/\alpha$ is the average distance measured in the direction of the electric force that two electrons move after the collision in which a molecule is ionized to the next collisions in which ions are again generated.

All the electrons do not act as indicated in fig. 4, since some of those entering the space between the planes x_1 and x_2 with small energies near the value $v/2$ may pass through without ionizing molecules, but the number passing out is made up to $2n_1$ by other electrons which enter the space with large energies near the value $c + v$ and ionize two molecules each. This does not alter the relation between the energies given by equation (4).

11. The quantities $\bar{v}$ and $\bar{w}$ are functions of the ratio X/p, and formula (4) represents the equation of the curve (fig. 3), giving α/p in terms of X/p.

The ratio X/α corresponding to different values of the ratio of X/p are found from the curve (fig. 3), and the quantity $(c + v/2 + w) = \cdot 693\mathrm{X}/\alpha$ is given in terms of X/p by curve 2 (fig. 2), the potential $\mathrm{V} = \cdot 693\mathrm{X}/\alpha$ being in volts, X in volts per centimetre, and p in millimetres of mercury. Thus the two quantities $c + \bar{v} + \overline{\mathrm{W}}$ and $c + \bar{v}/2 + \bar{w}$, corresponding to a series of values of the ratio X/p, are obtained directly from the experiments, the probable experimental error being about 2 or 3 per cent.

The difference between W and w is comparatively small. The quantity W represents the average loss of energy of an electron in collisions with molecules that are not ionized in moving from the negative electrode to the plane where its energy is $c + v$. The quantity w is the average loss of energy of an electron under the same conditions in moving from a plane where its energy is $\bar{v}/2$ to the same plane where its energy is $(c + v)$. Thus the difference $(\overline{\mathrm{W}} - w)$ is the loss

of energy of an electron in collisions with molecules in its path from the negative electrode to the point where its energy is $v/2$. In this part of its path the kinetic energy of the electron is comparatively small and the velocity in the direction of the electric force is comparatively large. As it moves in the direction of the electric force, the kinetic energy (which is the energy of agitation) increases and the velocity in the direction of the force diminishes. Thus, in the first part of its path from the negative electrode, the loss of energy of the electron in each collision is small and the total number of collisions per millimetre in the direction of the force is also small, since the latter number is proportional to the ratio of the velocity of agitation to the velocity in the direction of the electric force.

For a first approximation, therefore, the quantity $(\overline{W}-w)$ may be neglected in comparison with $\overline{w}$.

The following table gives the values of $\bar{v}$ and $(c+\overline{w})$ in volts obtained from the values of $(c+v+\overline{W})$ and $(c+v/2+w)$, taking $W=\overline{w}$:—

X/p.	$\bar{v}$.	$c+\overline{w}$.
5	15	21
10	17·6	14·4
16	18·6	12·9
30	25	10·0
47·5	31·8	9·5

12. The figures in the table confirm the obvious explanation of the phenomena indicated by the form and relative positions of the curves shown in fig. 1, or by the curve (fig. 3). Both methods of investigation lead independently to the conclusion that with a constant force X the loss of energy w increases with the pressure, and the average energy $(c+\bar{v})$ in the collisions which result in ionization increases as the pressure is reduced.

The figures in the column $(c+\overline{w})$ show that the energy c required to ionize a molecule of helium does not exceed 10 volts.

The smallest value of the energy $(\bar{v})$ is obtained with the smallest value of the ratio X/p. Since $\bar{v}$ represents an average energy, some molecules must be ionized in collisions where the energy of the electron is less than 25 volts. The curves (fig. 1) indicate that molecules are ionized in some cases when the energy $(c+v)$ of the electron is less than 22 volts.

It appears, therefore, that the kinetic energy of the electron must be at least twice the energy required to ionize a molecule in order that ionization may actually take place to an appreciable extent.

13. The results differ from the conclusions to which physicists have been led by applying the quantum theory to determine the transformations of energy which occur when electrons with comparatively small energy, of the order of 20 volts, collide with molecules. These conclusions are founded on the hypothesis that what may be a possible transformation of energy is, in fact, a transformation which is likely to occur in a large proportion of the total number of collisions in which the energy of the electron slightly exceeds a certain critical value. This theory has led to the conclusion that a large amount of energy is transferred from an electron to a molecule when the energy of the electron before the collision exceeds certain critical values V_1, V_2, &c. called resonance potentials. Having absorbed one of these quantities of energy, the molecule is then in a partially ionized state, or in a state in which it may emit radiation having a frequency proportional to V_1 or V_2, &c. In addition there is the potential V_i, which is greater than the resonance potentials and represents the energy required to ionize a molecule. When the energy of an electron exceeds this value, it ionizes a molecule ; but this conclusion is qualified by some supporters of the theory, who are of opinion that ionization may not occur in all cases when the energy of the electron exceeds the value V_i. The general impression is that molecules are ionized in a large proportion of such collisions.

Several experiments have been interpreted as supporting these conclusions ; but the evidence is not very convincing, and various values have been found for the critical potentials. For example, some experiments have been interpreted as indicating that the ionization potential in helium is 29·3 volts, as given by Bohr's calculations ; but the evidence of other experiments indicated that this potential is 20 volts. Many supporters of the theory state that this ionizing potential is 25 volts, and that the resonance potentials are between 20 and 25 volts for helium, so that we may adopt these numbers in considering the theory in connexion with the experiments we have described.

14. The most elementary experiments are those in which the initial effects of ionization by collision are investigated. When an electron starts from the negative electrode and moves under an electric force through the gas, it must make

several collisions with molecules when its energy is above the resonance potential V_1 before attaining the ionizing potential V_i. Whatever be the values of these potentials, the probability of losing energy in amounts corresponding to resonance potentials is greater than the probability of ionizing a molecule. The quantities of energy W and $\bar{w}$ lost in collision with molecules which are not ionized would therefore be comparable with the energy e lost in ionizing one molecule, and since the minimum value of $(e+\bar{w})$ is about 10 volts, the quantity e would under these circumstances be much less than 10 volts.

In cases where the pressure of the gas is high, as in some of the experiments represented by the curves (fig. 1) where the electrons make a large number of collisions with molecules, it has been suggested that the electrons never attain the energy corresponding to the ionization potential, but that molecules are ionized as a result of two collisions. Thus, when an electron with the energy 20 volts corresponding to one of the resonance potentials collides with a molecule, the molecule is partly ionized, and is completely ionized in another collision by an electron with an amount of energy corresponding to 5 volts. This may occur to an appreciable extent when the currents are large, but in these experiments the number N of electrons which pass through the gas from the negative to the positive electrode is so small that the number of molecules which could be ionized by this process is less than $N \times 10^{-6}$. Also, with small currents the number of molecules ionized by this process would be proportional to N^2; and as it has been found that the curves in figs. 1 and 3 are independent of the number N, the number of molecules which may be ionized as a result of two collisions must be inappreciable. The increase in conductivity which has been observed must therefore be attributed to ionization by single collisions.

With the pressures and forces used in these experiments, electrons make several collisions with molecules while moving with velocities less than that corresponding to 25 volts, but greater than the potentials corresponding to resonance. If they lost their energy in these collisions they never could attain their ionizing potential. The statements frequently made as to the loss of energy of electrons in amounts corresponding to resonance potentials are inconsistent with these experiments and similar experiments made with other gases.

It appears from this investigation that electrons moving with velocities corresponding to resonance potentials very rarely lose their energy when they collide with molecules.

XXXIII. *A Tentative Theory of the Capture and Loss of Electrons by Swift Nuclei.* *By* R. H. Fowler, *Fellow and Lecturer in Mathematics in Trinity College, Cambridge* *.

§ 1. *Introduction. The experimental facts.*—The phenomena of capture and loss of electrons by swift α-particles, first detected by Henderson †, have recently been studied in some detail by Rutherford—his results have just been published ‡. He establishes that when a beam of α-particles of given velocity emerges from a thin foil, the beam is not homogeneous but consists in general of a mixture of He^{++}, He^{+} and even He. The last named are only present to a noteworthy extent at the lowest velocities examinable by the scintillation method, and we shall not in general refer further to them in this paper. The emergent beam consists then of He^{++} and He^{+} present in a definite ratio, which depends on the velocity of the α-particles. The ratio further does not depend to any marked extent on the material of the foil, though there is a perceptible tendency for the number of He^{+} to be greater for gold foils than for foils of lighter elements. It is thus clearly established that the action of the thinnest foil is to set up a definite equilibrium ratio between He^{++} and He^{+} in the beam, which is a rapidly varying function of the velocity of the beam and almost independent of all other conditions.

These phenomena are only observable with a very good vacuum in the deflecting chamber in which the beam is analysed by the usual strong magnetic field. The phenomena which occur when gas is admitted are very significant. The first effect is to wipe out altogether the He^{+} particles, showing that they have lost their electron in a gas collision and have not in general picked one up again for an appreciable distance. A closer examination of the distribution of the scintillations shows, however, that at suitable gas pressures an appreciable number of both captures and losses do take place along the long path of the α-particle through the analysing chamber. This is established by the marked narrowing of the main band due to He^{++}. The slow over-deflected α-particles have an average charge of less than 2 when they have reasonable chances of capture, and therefore are less over-deflected when gas is admitted, relatively to the normal ones.

The ratio of the numbers of He^{++} to He^{+} varies with the

* Communicated by the Author.

† Henderson, Proc. Roy. Soc. A. cii. p. 496 (1922).

‡ Rutherford, *supra*, p. 277.

velocity over a wide range as a power of the velocity somewhere between 4·6 and 5. This variation has been tested from about the velocity of the α-particle from RaC ($1{\cdot}922 \times 10^9$ cm./sec., or 1040 equivalent electron-volts) down to α-particles of about 1/10 this energy, say 100 volts. At the top velocity (more precisely 1080 volts obtained with α-particles from ThC) the numerical value of the ratio is about 330, falling to 1 at the lower. The precise figures will be discussed later.

The equilibrium concentration ratio $[He^{++}]/[He^{+}]$ in the beam is expressed by Rutherford in another form. He points out that if λ_c is the mean free path for capture and λ_l the mean free path for loss in the foil, then

$$[He^{++}]/[He^{+}] = \lambda_c/\lambda_l. \quad . \quad . \quad . \quad . \quad (1)$$

He then shows that since the ratio λ_c/λ_l is practically independent of the nature of the foil, it will probably be the same in the gas. In the gas λ_l can be determined absolutely by observing the gas pressure required to abolish the He^{+} band. The actual value of λ_l, the free path for loss, is about that to be expected from our knowledge of the general process of ionization by collision and varies in the expected way with the velocity. The experiments thus determine absolutely both λ_c and λ_l. In the following sections we put forward a tentative theory of the action, which accounts roughly, even quantitatively for the observed facts.

§ 2. *A crude application of the theory of thermodynamic equilibrium.*—The nature of the equilibrium ratio established by Rutherford and its rough independence of almost everything except velocity suggests that this equilibrium ratio may conceivably represent roughly the ratio of the equilibrium concentrations of He^{++} and He^{+} which would be observed in a suitable gaseous assembly in thermodynamic equilibrium. So far as the relative interaction of the α-particle and an atom or electron is concerned, only the relative motion is relevant. It makes no difference therefore to the relative orbits whether we consider the α-particle or the atom and its electrons in motion. Let us contemplate then fixed or nearly fixed α-particles bombarded by a stream of swift atoms. So far as the vast majority of such interactions are concerned the effect of the nucleus of the bombarding atom may not be serious, and the interaction with any or all of the lightly bound electrons in such an atom must clearly be very much the same as if they were a cloud of free electrons of the same density in space. We may suppose in this

connexion that an electron is "lightly bound" if the energy required to remove it from the atom is a fairly small fraction of its equivalent energy as a member of the swarm. We are thus led to suppose that as a first very crude approximation most of the interactions between the α-particle and the atoms of the foil which result in captures or losses will take place just as in a gaseous assembly at a temperature which makes the mean energy of an electron equal to that of an electron with the speed of an α-particle, and at an electron density which is that of the lightly bound electrons in the foil.

The dissociative equilibrium, $He^+ \rightleftarrows He^{++} + \text{electron}$, is governed by well-known laws. If we may suppose that the He^+ can only exist with its electron in the final (normal) one-quantum orbit,—this will be examined more closely later on—then the equilibrium state is *

$$\frac{[He^{++}]P_e}{[He^+]} = \frac{0{\cdot}332}{2} T^{5/2} e^{-\chi/kT}. \quad . \quad . \quad . \quad (2)$$

In this equation χ is the ionization potential of normal He^+ (54 volts), P_e is the partial electron pressure, and k is Boltzmann's constant. To find the temperature T we have to equate $\frac{3}{2}kT$, expressed in volts, to W the speed of the α-particle in the same units. For this purpose we have

$$kT \textit{ volts} = 8{\cdot}60 \times 10^{-5} T, \ (T \textit{ in } {}^\circ C.).$$

Formula (2) refers to P_e, and we require ν_e the electron density which is given by

$$P = \nu_e kT. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Thus we take for the equilibrium law

$$\frac{[He^{++}]\nu_e}{[He^+]} = \frac{0{\cdot}332}{2k} T^{3/2} e^{-\chi/kT},$$

$$= 8{\cdot}25 \times 10^{20} W^{3/2} e^{-81/W}, \quad . \quad . \quad (4)$$

where W is the speed of the α-particle in volts. It is interesting to note that the temperature corresponding to 1040 volts is about 5,800,000° C.

Electron densities in foils can be fairly easily calculated. For Al the L-electrons are bound with about 70–80 volts †. We may probably take Al to have 11 electrons effectively

* See, for example, Fowler and Milne, Monthly Notices R. A. S. lxxxiii. pp. 407, 408 (1923).

* Here and elsewhere the data for the energy levels are taken from Bohr and Coster, *Zeits. f. Phys.* xii. p. 350 (1923).

free at all the higher speeds concerned, diminishing somewhat at the lower velocities. The density of the metal is 2·70 and the mass of an atom $27 \times 1{\cdot}662 \times 10^{-24}$ gm. Thus

$$\nu_e(\mathrm{Al}) = 6\ 6 \times 10^{23}.$$

For Ag the N- and O-level electrons, 19 in all, will be free at all the higher speeds; of these, 13 are bound with 45 volts or less, and 6 with about 100 volts. The M- (and other) level electrons which are bound with at least 370 volts, will be practically always permanently bound. Thus

$$\nu_e(\mathrm{Ag}) = 1{\cdot}11 \times 10^{24}$$

at the higher speeds, with much the same proportional diminution as for Al. For Au the electrons of the N_{VI}-, N_{VII}-, O-, and P-levels are similarly free, 27 in all, while the others are similarly bound. Thus

$$\nu_e(\mathrm{Au}) = 1{\cdot}59 \times 10^{24},$$

with similar variations. A substance like Cellulose $C_6H_{10}O_5$ seems to lead to an electron density about 4×10^{23}. Mica is difficult to calculate for exactly, but there is every reason to anticipate a result very little different from ν_e(Al). The electron densities thus calculated are very uniform, showing merely a slight increase with atomic weight. If as a rough figure we accept $\nu_e = 6{\cdot}6 \times 10^{23}$, we have

$$[\mathrm{He}^{++}]/[\mathrm{He}^{+}] = 1{\cdot}25 \times 10^{-3} W^{3/2} e^{-81/W}, \quad (W \textit{ volts}).$$

We arrive at once at

$$W = 1000, \quad [\mathrm{He}^{++}]/[\mathrm{He}^{+}] = 40,$$
$$W = 100, \quad [\mathrm{He}^{++}]/[\mathrm{He}^{+}] = 0{\cdot}56.$$

The corresponding experimental figures are about 1 and 330. The agreement with this extremely rough calculation is amply sufficient to encourage us in thinking that we are discussing the phenomenon on the right lines and in attempting to better the theory by re-examining it with the help of some definite mechanism by which the captures and losses may be effected. In the light of the above agreement the mechanism may be supposed to be one which, in an ordinary assembly, will set up exactly the ordinary equilibrium laws.

One further salient point remains to be considered—that is that the ratio of the free paths for capture and loss seems to be the same in the foil and in a dilute gas. In the light of (2) no such state of affairs could possibly hold good if P_e or ν_e refer to the *general* electron pressure or density. We must suppose, and this is in agreement with all the

weight of other evidence, that the ν_e of the formula is the ν_e *inside an atom or molecule*, and that in any case of capture or loss the whole of the interaction is provided by the electrons (or perhaps electrons and nuclei) belonging to a single atom or molecule. The rest of space can as it were be wiped out; nothing whatever happens there. On this view, which seems in any case to be correct, our preceding calculations for foils will not be substantially affected, for the ν_e for atoms and the ν_e for metallic foils or mica slips are not greatly different. The former may be larger by a factor of 2 or 3. The calculations will thus apply at once to similar atoms in a gaseous as well as in a solid state.

§ 3. *Application of the theory of capture and loss by electronic collision in gaseous assemblies in statistical equilibrium.*—As a result of the foregoing considerations we must treat the $[He^{++}]/[He^{+}]$ equilibrium as equivalent to the thermodynamic or statistical equilibrium of a gaseous assembly at high temperature, modified by certain peculiar circumstances, of which obviously the most important is the fact that all the electrons have about the same velocity relative to the α-particles instead of velocities distributed according to Maxwell's Law. We are going to use as an analogy to the process of capture and loss by flying α-particles the ordinary processes of capture and loss which certainly govern the state of an assembly in genuine dissociative equilibrium. To apply the laws of such processes to this distorted case we must have a knowledge of these laws in certain detail. This knowledge of detail is available to a sufficient extent to make a start on the problem of the α-particle.

In an ordinary assembly captures and losses can take place by two main mechanisms—radiative or non-radiative—the latter in the simplest case are collisions in which at one stage or another three bodies are concerned—for example, an He nucleus and two electrons. We shall consider at a later stage the evidence that leads one to believe that the processes of capture and loss of electrons by α-particles are essentially non-radiative. It is possible to work out the laws of capture and loss by the simplest collisions in exactly the same way as Klein and Rosseland * have worked out the laws of collisions of the first and second kind †. The process of loss is merely ionization by electronic impact. It is there shown that the associated reverse process must be assumed

* Klein and Rosseland, *Zeits. f. Phys.* iv. p. 46 (1921).
† Fowler, *supra*, p. 257.

to be a three-body collision in which one electron is bound by the atom, and the other goes off with all the superfluous energy. The number of a definite type of ionizations by collision per cubic centimetre per second may be written

$$x_1\left(\frac{2\epsilon}{m}\right)^{1/2}\mu(\epsilon)\,d\epsilon\,S_1^2(\eta,\epsilon)\,d\eta: \quad . \quad . \quad . \quad . \quad (5)$$

this is the number due to electrons with energy between ϵ and $\epsilon+d\epsilon$ (ϵ-electrons), which results in knocking out an η-electron. If ϵ_0 is the ionization potential $S_1^2(\eta,\epsilon)\equiv 0$, when $\epsilon<\epsilon_0+\eta$. The number of captures per cubic centimetre per second in which a ζ-electron is bound by the interaction of a ξ-electron is similarly

$$x_2\left(\frac{2\zeta}{m}\right)^{1/2}\mu(\zeta)d\zeta\left(\frac{2\xi}{m}\right)^{1/2}\mu(\xi)d\xi\,S_2^1(\zeta,\xi). \quad . \quad . \quad (6)$$

Here x_1 and x_2 are the concentrations of atoms and ions (or He^+ and He^{++}) respectively and $\mu(\zeta)d\zeta$ is Maxwell's distribution law for electrons. To preserve the usual laws of statistical equilibrium it is further shown that we must have for all α and η

$$(\epsilon_0+\eta+\alpha)S_1^2(\eta,\epsilon_0+\eta+\alpha)=\frac{8\pi m\sigma}{qh^3}\alpha\eta S_2^1(\eta,\alpha). \quad . \quad (7)$$

In equation (7) and elsewhere m is the mass of the electron, σ is the number of equivalent electrons removable with expenditure of work ϵ_0, q is the "weight" of the atom in its normal state relative to the ion, and h is Planck's constant.

It is further shown on the basis of the classical ionization theory of J. J. Thomson that

$$S_1^2(\eta,\epsilon)=\frac{A\sigma}{\epsilon}\frac{1}{(\eta+\epsilon_0)^2}, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and therefore that

$$S_2^1(\eta,\alpha)=\frac{1}{\alpha\eta}\frac{qh^3}{8\pi m}\frac{A}{(\eta+\epsilon_0)^2}. \quad . \quad . \quad . \quad . \quad (9)$$

Equation (8) is substantially equivalent to the V^4-law for the ranges of β-particles, expressed in the present notation. It may be thought of here as fully equivalent to this law and of the same range of validity. Since we are concerned with only moderate velocities and fundamentally with only electron-electron interactions we do not require the relativity modifications.

On the strict classical theory $A=\pi e^4$. This value may be

too small by a factor of perhaps 2 or 3, but the exact value of A (provided it is constant) is only of secondary importance here.

If ionization by electronic impact and the associated reverse process form the mechanism which controls the equilibrium $[He^{++}]/[He^{+}]$ in the beam of α-particles, it is easy to deduce a much more precise theoretical value for this ratio on the basis of (6) and (7). As a first approximation we may suppose that all the electrons have an energy W, so that the electron distribution law here, instead of Maxwell's law, is

$$\mu(\epsilon)d\epsilon = \nu_e, \quad (\epsilon = W),$$
$$\mu(\epsilon)d\epsilon = 0, \quad (\epsilon \neq W).$$

The rate of production of He^{++} by ionization is therefore by (5) and (8)

$$[He^{+}]\left(\frac{2W}{m}\right)^{1/2} \nu_e \int_0^{W-\epsilon_0} \frac{A\sigma}{W} \frac{d\eta}{(\eta+\epsilon_0)^2},$$

or

$$[He^{+}]\nu_e \left(\frac{2}{mW}\right)^{1/2} A\sigma\left(\frac{1}{\epsilon_0} - \frac{1}{W}\right) \quad . \quad . \quad . \quad (10)$$

The rate of production of He^{+} by capture is by (6) and (9).

$$[He^{++}]\nu_e^2 \frac{2}{mW} \frac{qh^3}{8\pi m} \frac{A}{(W+\epsilon_0)^2}, \quad . \quad . \quad (11)$$

The equilibrium ratio must therefore be given by the equation

$$\frac{[He^{++}]\nu}{[He^{+}]} = \frac{8\pi m\sigma}{qh^3}\left(\frac{m}{2}\right)^{1/2} \frac{W-\epsilon_0}{W\epsilon_0} W^{1/2}(W+\epsilon_0)^2. \quad (12)$$

We observe at once that for values of W fairly large compared with ϵ_0 (54 volts) equation (12) predicts a variation

$$[He^{++}]/[He^{+}] \propto W^{5/2} \propto V^5, \quad . \quad . \quad . \quad (13)$$

which is in substantial agreement with Rutherford's observations ($V^{4\cdot6}$ or V^5). What is more, the actual numerical agreement is far better than could have been hoped. If we express all the energies in (12) in volts (1 volt $= 1\cdot591 \times 10^{-12}$ erg) and insert the usual numerical values $m = 9\cdot00 \times 10^{-28}$, $h = 6\cdot55 \times 10^{-27}$ and the values proper to He^{+}, $q=2$, $\sigma=1$, we find that

$$\frac{[He^{++}]\nu_e}{[He^{+}]} = 1\cdot71 \times 10^{21} \frac{W-\epsilon_0}{W\epsilon_0} W^{1/2}(W+\epsilon_0)^2, \ (W,\ \epsilon_0,\ volts).$$

. . . (13)′

If we take as a round figure $\nu_e = 10^{24}$, we obtain the following table for comparison with Rutherford's experimental values.

TABLE I.

W Volts.	$[He^{++}]/[He^{+}]$ Calc. $\nu_e = 10^{24}$.	$[He^{++}]/[He^{+}]$ Obs.	$[He^{++}]/[He^{+}]$ Calc. $\nu_e = 4 \times 10^{24}$.
1080	1270	330	320
920	860	200	215
600	300	67	75
230	30	7·5	7·5
100	3·5	1·0	0·9
90	2·6		0·65

The table shows that an excellent agreement between theory and experiment could be obtained if we were at liberty to suppose that ν_e had values of the order $3,4 \times 10^{24}$ for all velocities. These values are perhaps slightly high, particularly for low velocities. But they are probably to be modified in a downward sense in view of certain other considerations in the next section. The general conclusions would seem to be favourable to the theory.

§4. *A critical examination of the assumptions of the theory.*— It is well to pause at this stage and reconsider the basis of these results. We have assumed

(i.) That captures and losses take place inside an individual atom or molecule much as if the lightly-bound electrons were a free electron gas of equivalent density.

(ii.) That the mechanism of capture and loss is the ordinary mechanism of ionization by electronic impact together with the associated reverse process of radiationless three-body capture.

(iii.) That the part played by the core of the atom (nucleus + tightly-bound electrons) may be ignored.

(iv.) That in the case of He^{+} only the normal 1-quantum orbit is effectively present under the given conditions.

We have little or no reason to question the applicability of (i.) at the higher velocities. It is substantiated by any theory of ionization by α- and β-particles.

Under (ii.) we should notice that the coefficients S_1^2 and S_2^1 refer strictly to the conditions of gaseous assemblies in

which the electron velocities are distributed in all directions and are not almost unidirectional as here. Thus the S_1^2 and S_2^1 which we have used are really averages taken over all relative orientations of the axis of the atom, and the directions of motions of any incident electron or electrons. The unidirectional bombardment here may very well not affect S_1^2, but on the other hand it may equally well seriously affect S_2^1. If the capture process is really the reverse of the ionization process in every detail, the most effective relative direction of incidence for capture may well be nearly at right angles, since the electrons after ionization has occurred will in general be moving more or less at right angles. This effect should cut down captures and still further increase the ratio $[He^{++}]/[He^{+}]$ at high velocities, but by how much it would be far from easy to calculate.

In the same connexion we may point out that there is no need to make the stringent assumption that all the bombarding stream have velocities exactly equivalent to W volts. It is easy to allow for a combination of this with another velocity orientated in a random direction; this will represent approximately the motion of the electrons in the atom. For this purpose one must work primarily in velocities rather than energies. One then finds that if the velocity of the electron stream is V, and the orbital velocities v, then

$$\mu(\epsilon)d\epsilon = \frac{\nu_e}{2v}\frac{1}{(2m)^{1/2}}\frac{d\epsilon}{\sqrt{\epsilon}}, \quad (\tfrac{1}{2}m(V-v)^2 < \epsilon < \tfrac{1}{2}m(V+v)^2),$$
$$= 0, \quad (\epsilon > \tfrac{1}{2}m(V+v)^2,\ \epsilon < \tfrac{1}{2}m(V-v)^2).$$

The resulting integrals are still of simple forms and easily evaluated. One finds that ionizations now occur at a rate

$$[He^{+}]\nu_e \frac{A\sigma}{m}\frac{1}{v}\left[\frac{1}{\epsilon_0}\log\frac{V+v}{V-v} - \frac{4Vv}{m(V^2-v^2)^2}\right],$$

provided that $\frac{1}{2}m(V-v)^2 > \epsilon_0$, and captures at a rate

$$[He^{++}]\nu_e \frac{A}{m^2}\frac{qh^3}{8\pi m}\frac{1}{2v^2}\log\frac{V+v}{V-v}\cdot\left[\frac{2}{\epsilon_0^2}\log\frac{V+v}{V-v}\right.$$
$$-\frac{1}{\epsilon_0^2}\log\frac{\frac{1}{2}m(V+v)^2+\epsilon_0}{\frac{1}{2}m(V-v)^2+\epsilon_0} - \frac{1}{\epsilon_0}\left\{\frac{1}{\frac{1}{2}m(V-v)^2+\epsilon_0}\right.$$
$$\left.\left.-\frac{1}{\frac{1}{2}m(V+v)^2+\epsilon_0}\right\}\right].$$

The modified form for the rate of loss for $\frac{1}{2}m(V-v)^2 < \epsilon_0$ can easily be obtained when required. The formulæ are a

little complicated and numerical values must be inserted to estimate the effect. Taking the voltages corresponding to v and ϵ_0 as 25 and 50, and to V the values 900, 225, and 100, we find that the calculated values of $[He^{++}]/[He^{+}]$ are smaller by the factors 1/1·13, 1/1·58, and 1/2·8. These corrections have the effect of diminishing the ν_e necessary for agreement in Table I., and are of just the right nature to allow for a reasonable decrease in effective ν_e with decreasing velocity. One can scarcely push the correction further at this stage.

With reference to (iii.) we may observe that the neglect of the core is certainly not justifiable *a priori*. It should be possible to take account of it in just the same way as we have taken account of the "free" electrons on the basis of a mechanism of ionization and its reverse capture by means of collisions in which a heavily charged core knocks out electrons or helps to bind them in another atom. This requires, however, a knowledge of the relation analogous to (7) for the case in which two of the bodies are of comparable mass, which has not yet been worked out. We may observe, however, that we must expect to obtain relations of the same general type as (7), (8), and (9). The classical theory of the production of primary ionization by α-particles for example indicates a value for the new $S_1^2(\eta, \epsilon)$ closely analogous to (8). It is therefore very probable that even if the effect of the core is sufficient seriously to influence the individual rates of capture and loss, their ratio will be affected only to a secondary extent.

It must be pointed out that assumption (iv.) is open to question, although physically it would seem eminently reasonable. The arguments of statistical mechanics are based on the assumption of "limited interferences"—that is that any particular state of any atom or other system in general exists undisturbed in the assembly for times which are long compared with the times during which energy exchanges are taking place. All states for which this condition is fulfilled must be included, but it is not yet possible to say for certain where the line is to be drawn to exclude states other than these. An indication can, however, be obtained by considering how often on the average per revolution the electron will be removed from an orbit in He^{+} by electrons of velocity W and space density 10^{24}. The number of ionizations per atom per second is then

$$\nu_e \left(\frac{2}{m\mathrm{W}}\right)^{1/2} \mathrm{A}\left(\frac{1}{\epsilon_0} - \frac{1}{\mathrm{W}}\right), \quad . \quad . \quad . \quad . \quad (14)$$

which works out at about $2{\cdot}2 \times 10^{15}$ per sec. for the normal

1-quantum orbit and W = 1000. The orbital frequency for this orbit is $2{\cdot}6 \times 10^{16}$ as calculated from the ordinary formulæ. There is thus on the average one removal for every ten revolutions, which is a reasonably small amount of disturbance. But for an n-quantum orbit the ionization frequency is multiplied by n^2 and the orbital frequency by $1/n^3$. Thus the n-quantum orbit will exist undisturbed on the average for only $10/n^5$ revolutions. The 2-quantum orbit can exist on the average only for $\frac{1}{3}$ of a revolution, and every other orbit for a much smaller fraction. It is possible that we should think of the 2-quantum orbit (of weight 6) as being effective or partially effective. We can hardly expect any other orbits of higher quantum number than 2. This point of view is supported by the relative sizes of the orbits. The radius of the 1-quantum orbit is $2{\cdot}6 \times 10^{-9}$ cm., of the 2-quantum orbit $1{\cdot}06 \times 10^{-8}$ cm. The average distance apart of electrons at a density 10^{24} is about 10^{-8} cm.

What follows is exceedingly speculative, but perhaps suggestive. If in the corresponding assembly in statistical equilibrium He^+ in the 2-quantum orbit is to any degree effectively present, we must suppose it present here to the corresponding extent. Relations for capture and loss to and from the 2-quantum state will be formally the same as for the 1-quantum state with new values of q and ϵ_0. We obtain at once the analogue of (12),

$$\frac{[He^{++}]\nu}{[He^+]_2} = \frac{8\pi m\sigma}{q_2 h^3}\left(\frac{m}{2}\right)^{1/2} \frac{W - (\epsilon_0)_2}{W(\epsilon_0)_2} W^{1/2} (W + (\epsilon_0)_2)^2, \quad (15)$$

in which the suffix 2 denotes the 2-quantum state of the atom. Since $q_2 = 6$, $(\epsilon_0)_2 = \frac{1}{4}\epsilon_0$ we find very approximately from (12) and (15) that

$$\frac{[He^{++}]\nu_e}{[He^+] + [He^+]_2} = \frac{[He^{++}]\nu_e}{[He^+]} \times \frac{2}{2 + 1{\cdot}5}.$$

It is just possible that some part of the numerical discrepancy in Table I. may be properly and simply accounted for in this way. Further speculation, however, on these lines is hardly profitable at this stage, and we shall not assume any appreciable fraction of captures into a two or more quantum orbit in the rest of the discussion here.

§ 5. *The mean free path for loss*, λ_l.—The rate of loss of electrons per atom per second by the $[He^+]$ is given by (14). We derive the mean free path for loss λ_l by dividing the

velocity $(2W/m)^{1/2}$ by the expression (14). Thus

$$\lambda_l = \frac{W}{\nu_e A\left(\frac{1}{\epsilon_0} - \frac{1}{W}\right)} \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Thus makes $\lambda_l \propto V^2$, a law which is probably not exactly correct; Rutherford's experiments seem to make λ_l vary more nearly as V over the range $0{\cdot}94V_0$, $0{\cdot}47V_0$, where V_0 is the initial velocity of the α-particle from RαC. But this deviation is of course just the deviation from experimental fact inherent in all current theories of the ionization due to α-particles, and is not unexpected here. In (16) ν_e refers strictly to atomic interiors—no collisions of any sort occurring outside. To find, however, the numerical value of λ_l in air, say, we need only interpret ν_e in (16) as the ν_e of the air. It makes no difference to the average number of collisions leading to loss if the electrons causing the loss are distributed in dense clouds (atoms) or uniformly, provided the average electron density is the same. The resulting value of ν_e may be taken to be $10{\cdot}4 \times 2{\cdot}70 \times 10^{19}$ per cubic centimetre for air at normal pressure and temperature. The average number of loosely bound electrons in the air molecule is 10·4. We thus find

$$\lambda_l = 3{\cdot}47 \times 10^{-8} \frac{W^2\epsilon_0}{W - \epsilon_0}. \quad (W, \epsilon_0, \textit{volts}) \quad . \quad (17)$$

The observed and calculated values of λ_l are given in Table II.

TABLE II.

Velocity in terms of V_0.	Velocity in volts.	λ_l obs. mm.	λ_l calc. mm.
0·94	920	0·011	0·019
0·76	600	0·0078	0·013
0·47	230	0·0050	0·0058

The agreement is very satisfactory. In this calculation there is no possible doubt as to ν_e. One would perhaps have expected the calculated λ_l to exceed the observed λ_l by a somewhat greater factor than it does, as there is the effect of the hard core to be allowed for. But we may rest content with Table II. at this stage.

§ 6. *The equilibrium ratio* $[H^+]/[H]$ *in a beam of positive rays.*—It has recently been shown by Rüchardt *, in some very convincing experiments, that in a beam of hydrogen positive rays travelling through various gases a definite equilibrium ratio $[H^+]/[H]$ is set up, which varies rapidly with the velocity. The H^+ particles had been accelerated by fields varying from 36,000 to 16,000 volts, so that their equivalent velocities are only from 19·5 to 8·5 volts, and are very low for the applicability of the present method. For the highest velocities the theory should still perhaps be roughly applicable. Rüchardt gives the following values:

$$\begin{aligned}[H^+]/[H] &= 0{\cdot}51 \text{ at } 19{\cdot}5 \text{ volts in } H_2,\\ &= 0{\cdot}89 \text{ at } 18{\cdot}7 \text{ volts in } N_2,\\ &= 1{\cdot}02 \text{ at } 19{\cdot}8 \text{ volts in } O_2.\end{aligned}$$

We have to apply formula (13)′, the only difference being that now $\epsilon_0 = 13{\cdot}54$ volts. We thus obtain

$$\begin{aligned}[H^+]\nu_e/[H] &= 1{\cdot}9 \times 10^{23} \text{ at } 19{\cdot}5 \text{ volts},\\ &= 1{\cdot}6 \times 10^{23} \text{ at } 18{\cdot}7 \text{ volts},\\ &= 2{\cdot}0 \times 10^{23} \text{ at } 19{\cdot}8 \text{ volts}.\end{aligned}$$

The ratios will agree at the top velocities with Rüchardt's observations if we have molecular electron densities

$$\begin{aligned}\nu_e &= 3{\cdot}7 \times 10^{23} \text{ in } H_2,\\ \nu_e &= 1{\cdot}8 \times 10^{23} \text{ in } N_2,\\ \nu_e &= 2{\cdot}0 \times 10^{23} \text{ in } O_2.\end{aligned}$$

Since only the most lightly-bound electrons can be concerned (17 volts at the very most) these figures are not inconsistent among themselves and are not inconsistent with a value of $\nu_e = 10^{24}$ for higher velocities. At the same time we have obviously already strained the theory to the breaking point in applying it to these very low velocities. That agreement still persists to this extent is eminently satisfactory. We may observe finally that the V^5-law still seems to persist in this region for the observations in H_2 and O_2. The observations in N_2 are hardly consistent, for they show a quite different and much slower variation.

§ 7. *General Discussion.*—The foregoing considerations, incomplete as they unfortunately are, seem to indicate that

* Rüchardt, *Ann. der Phys.* lxxi. p. 377 (1923).

the controlling mechanism by which the equilibrium ratio is set up in the beam of α-particles is a mechanism of loss and capture by collision processes of a definite type. In arriving at this conclusion we have found it desirable to consider the α-particles as at rest and the electrons as in motion with the appropriate velocity. This is of course legitimate here, for it is only the relative motion that affects the processes of capture or loss which can be referred directly to the circumstances of the relative orbit. It is of course equally true that the actual exchanges of energy between the particles depend on the absolute velocities, not merely on the relative velocity. This must be borne in mind in forming a detailed physical picture of the action of these mechanisms.

We have not here discussed the possibility of a radiative mechanism of capture. It appears to me however, that, as far as this can be discussed at present, it leads to a wrong variation with velocity. The number of captures per He^{++} per second varies here as $1/V^6$, the mean free path for capture as V^7. It appears that Kramer's* calculations lead to a chance of capture by radiation in any single encounter which varies as $1/V^4$. The captures per He^{++} per second by this mechanism vary therefore as $1/V^3$ and the free path as V^4. In view of this discrepancy I have not used Kramer's results to calculate the absolute rate of capture by radiation at any velocity. The experimental facts on velocity variation are sufficient to establish that radiative captures play only a subordinate part.

It is perhaps here permissible to stress certain points suggested by the theory as likely to repay further investigation. The quantity ν_e, the intra-atomic "free" electron density, plays a fundamental part in the theory. If the theory is in any way correct the equilibrium ratio $[He^{++}]/[He^{+}]$ ought to vary from foil to foil like $1/\nu_e$. We can be fairly certain *a priori* of the relative values of ν_e for different atoms for a given velocity. A detailed experimental investigation of this variation at a number of velocities would provide a fairly crucial test of the theory. It would further prove of great interest to examine, if it is possible, the equilibrium ratio for swift H^{+}- and H-particles ; one would thus extend Rüchardt's investigations to a range of velocities of H-particles only attainable by collision with α-particles, at which the theory and observations are more directly comparable. One should thus be able to test with more

* Kramers, Phil. Mag. xlvi. p. 836 (1923).

certainty the predicted variation of the equilibrium ratio with ϵ_0. From the general theoretical point of view every possible examination of the theory is of the greatest interest. For the theory itself is of the nature of an extrapolation of statistical arguments to the conditions holding in an assembly at some 5,800,000° C. Gaseous assemblies such as these most certainly exist—the interiors of giant stars for example may be at even greater temperatures. To these we may hope to apply all the statistical ideas which have been and are now being developed. But any direct check on the theory, such as is provided by the present experiments, is of the greatest value in guaranteeing that our extrapolations of statistical mechanics to such assemblies have not, in some unexpected way, exceeded the range of validity.

§ 8. *Summary.*—The equilibrium ratio of the concentrations of He^{++} and He^{+} in a beam of α-particles of given velocity is discussed in the light of Sir E. Rutherford's experiments.

It is shown that the equilibrium is probably of the nature of a thermodynamic equilibrium corresponding to an electron density equal to that of the lightly bound electrons in the interior of an atom [perhaps 2×10^{24} per c.c.] and a temperature equal to that at which electrons have on the average the velocity of the α-particle [5,800,000° C. for the initial velocity of α-particles from RaC].

The mechanism of capture and loss is probably a collision-mechanism (non-radiative). Loss corresponds to ionization by electronic impact—capture to the strict reverse of this, a three-body collision. The ratio of the frequencies of such processes has been recently established by the author as an extension of the ideas of Klein and Rosseland. This ratio leads at once roughly to the observed equilibrium when it is applied to the conditions of the experiments on α-particles.

In conclusion it is a pleasure to thank Sir E. Rutherford for information supplied in advance of publication, and for many valuable critical discussions at all stages of the development of the theory.

XXXIV. *On a proposed Empirical Equation of State for Fluids.* *By* S. Lees, *M.A., St. John's College, Cambridge* *.

Introduction.

§ 1. MANY investigators have devoted attention to the problem of framing an adequate equation of state for fluids in general. (By equation of state is meant a relation which must always be satisfied between the pressure p, volume V, and absolute temperature T for unit mass of a fluid.) Reference may here be made to the equations of van der Waals †, Clausius †, Dieterici †, Porter ‡, and others. Whilst there are objections on individual points to all of these equations, each of them has had success in certain directions in helping to rationalize the behaviour of gases and vapours.

In addition to the above-mentioned equations, which have some application for all values of the variables p, V, and T, reference may be made to others (*e.g.*, that of Callendar for steam, and that of D. Berthelot § for low pressures) which are intended to have but a restricted field or range of application for the variables. Such restricted equations of state have been extremely useful in compiling tables of properties of particular fluids for technical purposes.

In the following paper the author endeavours to develop an equation of the unrestricted type, and some apology may seem to be required for adding another to the existing equations of this type. The author is of opinion, however, that the equation he has to propose is simple in form, and of interest as agreeing on certain points more closely with experimental facts than other proposed (simple) formulæ. It is not claimed that the proposed equation has important esoteric significance. The method, in fact, which has been followed in connexion with this paper may be described as "formula-fitting," with a fairly frequent comparison with the experimental facts.

* Communicated by the Author.

† General reference may be made to Kuenen, *Die Zustandsgleichung der Gase und Flüssigkeiten*; also to H. Kamerlingh Onnes and W. H. Keesom, *Die Zustandsgleichung* (Art. v. 10, *Encyklopädie der Math. Wissenschaften*; reprinted in Communications from the Physical Laboratory of Leiden).

‡ Phil. Mag. xliv. p. 1020 (1922).

§ *Trav. et Mém. du Bur. Internat.* xiii. (1907).

Type of Equation of State chosen.

§ 2. In building up an equation of state, certain assumptions are made in this paper. There is, firstly, the assumption that at high temperatures and low pressures, *i. e.* with large specific volumes V, the equation approaches asymptotically the perfect gas equation

$$pV=RT, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where R is the gas constant for unit mass. When this condition is satisfied, the fluid is sometimes said to be in the Avogadro-state. Secondly, it is assumed that at large pressures and low temperatures the volume V tends to a limit b which is to all intents and purposes identical with the volume of the fluid in the liquid condition.

Guided by these assumptions, the general type of equation of state has been taken as*

$$[p+\phi(p, V, T)] . (V-b)=RT, \quad . \quad . \quad . \quad (2)$$

where $\phi(p, V, T)$ is a function to be investigated and if possible to be determined. It may be noted that ϕ (by assumption) must tend to zero as V is made indefinitely large. It must also be such as not to interfere with the validity of the second of the above assumptions.

Critical Phenomena.

§ 3. A further and most important restriction on ϕ is that it must allow of the existence of critical phenomena. Assuming that this is the case, we shall have at the critical point

$$\left(\frac{\partial p}{\partial V}\right)_T=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T=0. . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

From (2) we have

$$p=\frac{RT}{V-b}-\phi(p, V, T),$$

* The novel feature of this equation lies in making ϕ a function of the *three* variables p, V, and T. The usual theoretical interpretation of the factor $(V-b)$ would be that the volumes of the molecules (taken as proportional to b) are invariable.

and hence *

$$\left(\frac{\partial p}{\partial \mathrm{V}}\right)_{\mathrm{T}} = \frac{-\mathrm{RT}}{(\mathrm{V}-b)^2} - \frac{\partial \phi}{\partial \mathrm{V}} - \frac{\partial \phi}{\partial p}\left(\frac{\partial p}{\partial \mathrm{V}}\right)_{\mathrm{T}},$$

$$\left(\frac{\partial^2 p}{\partial \mathrm{V}^2}\right)_{\mathrm{T}} = \frac{2\mathrm{RT}}{(\mathrm{V}-b)^3} - \frac{\partial^2 \phi}{\partial \mathrm{V}^2} - \frac{2\partial^2 \phi}{\partial p \partial \mathrm{V}}\left(\frac{\partial p}{\partial \mathrm{V}}\right)_{\mathrm{T}} - \frac{\partial \phi}{\partial p}\left(\frac{\partial^2 p}{\partial \mathrm{V}^2}\right)_{\mathrm{T}}.$$

Equations (3) and (4) thus reduce to the simple results for the critical point

$$\frac{\partial \phi}{\partial \mathrm{V}} = \frac{-\mathrm{RT}}{(\mathrm{V}-b)^2}, \quad \ldots\ldots \quad (5)$$

$$\frac{\partial^2 \phi}{\partial \mathrm{V}^2} = \frac{+2\mathrm{RT}}{(\mathrm{V}-b)^3}, \quad \ldots\ldots \quad (6)$$

which, it will be noticed, do not at all involve explicitly the dependence of ϕ on p or T.

We now make the additional assumption † that $\phi(p, \mathrm{V}, \mathrm{T})$ can be expressed as $\frac{1}{\mathrm{V}^n}\psi(p, \mathrm{T})$, where n presumably will be positive to preserve the first of the assumptions of § 2.

In this case, we have $\partial\phi/\partial \mathrm{V} = -n\psi/\mathrm{V}^{n+1}$, $\partial^2\phi/\partial \mathrm{V}^2 = n(n+1)\psi/\mathrm{V}^{n+2}$. Substituting these values in (5) and (6), and dividing the latter of these by the former, we obtain

$$\frac{n+1}{\mathrm{V}} = \frac{2}{\mathrm{V}-b},$$

$$i.e. \qquad \mathrm{V}_c = (n+1)b/(n-1). \quad \ldots\ldots \quad (7)$$

The suffix c has been attached to V in (7) to indicate that we are referring solely to the critical volume.

In applying this result to determine n, it is assumed that the correct experimentally determined mean value of V_c is $4b$. This would appear to be very nearly the case ‡. In passing, it may be noted that van der Waals' equation makes $\mathrm{V}_c = 3b$, whilst the equation of Dieterici gives $\mathrm{V}_c = 2b$.

Substituting then $\mathrm{V}_c = 4b$ in (7), we find $n = 5/3$. This

* In the differential coefficients of ϕ, only the independent variables indicated are supposed to vary. This is the usual notation.

† By using here a single power of V, and later in §§ 4 and 5 single powers of p and T respectively, we are assured of the equation of state satisfying the principle of corresponding states (see § 6).

‡ See, *e.g.*, Lewis, 'System of Physical Chemistry,' 1918, vol. i. p. 80.

may be compared with the value $n=2$ used in van der Waals' equation.

The obtained value of n $(=5/3)$ is supported in the strongest manner by the consideration of the ratio of RT_c/p_cV_c. We find from (5)

$$RT_c=n\psi_c(V_c-b)^2/V_c^{n+1}. \quad . \quad . \quad . \quad . \quad (8)$$

If this be used to eliminate ψ_c in

$$p_c=\frac{RT_c}{V_c-b}-\frac{\psi_c}{V_c^n},$$

we find

$$p_c=\frac{RT_c}{(V_c-b)^2}\left[V_c\left(1-\frac{1}{n}\right)-b\right]. \quad . \quad . \quad (9)$$

If, as before, we assume $V_c=4b$, we find $p_c=RT_c(3-4/n)/9b$. Hence

$$\frac{RT_c}{p_cV_c}=\frac{RT_c}{4bp_c}=9/4(3-4/n). \quad . \quad . \quad . \quad . \quad (10)$$

We shall take the experimentally determined mean value of this ratio * to be 15/4. In this connexion, it may be noted that whilst Dieterici's equation gives for this ratio about 3·7/1, the equation of van der Waals gives for the ratio 8/3.

Substituting 15/4 for RT_c/p_cV_c in (10), we find $n=5/3$ as before. This seems a remarkable result †.

We may sum up the results of this section by stating that if the equation

$$\left[p+\frac{\psi(p,T)}{V^{5/3}}\right](V-b)=RT, \quad . \quad . \quad . \quad (11)$$

where $\psi(p,T)$ is as yet undetermined, gives a critical point, then at this critical point $V_c=4b$, and $RT_c/p_cV_c=15/4$; both of which results are in good agreement with experiments on a large number of gases.

Variation of the product pV.

§ 4. We proceed to discuss the variation of the product pV along an isothermal $T=$constant.

If we write (11) in the form

$$p=\frac{RT}{V-b}-\frac{\psi}{V^{5/3}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11a)$$

* See Lewis, *loc. cit.* p. 79.

† An alternative procedure for this section is to assume

$$\phi=\psi(p,T)/(V-C)^n,$$

where c is a constant. We then find $c=0$ and $n=5/3$ as before.

we get on differentiation with respect to V (keeping T constant)

$$\left(\frac{\partial p}{\partial \mathrm{V}}\right)_{\mathrm{T}} = \frac{-\mathrm{RT}}{(\mathrm{V}-b)^2} + \frac{5\psi}{3\mathrm{V}^{8/3}} - \frac{1}{\mathrm{V}^{5/3}}\frac{\partial \psi}{\partial p}\left(\frac{\partial p}{\partial \mathrm{V}}\right)_{\mathrm{T}},$$

i. e.

$$\left(\frac{\partial p}{\partial \mathrm{V}}\right)_{\mathrm{T}} = \left[\frac{-\mathrm{RT}}{(\mathrm{V}-b)^2} + \frac{5\psi}{3\mathrm{V}^{8/3}}\right] \Big/ \left[1 + \frac{\partial \psi}{\partial p}\Big/ \mathrm{V}^{5/3}\right] \quad . \quad (12)$$

Multiplying the right-hand side of (11 *a*) by V to get the value of $p\mathrm{V}$, we find on differentiation with respect to V along T = constant

$$\left[\frac{\partial(p\mathrm{V})}{\partial \mathrm{V}}\right]_{\mathrm{T}} = \frac{-b\mathrm{RT}}{(\mathrm{V}-b)^2} + \frac{2\psi}{3\mathrm{V}^{5/3}} - \frac{1}{\mathrm{V}^{2/3}}\frac{\partial \psi}{\partial p}\left(\frac{\partial p}{\partial \mathrm{V}}\right)_{\mathrm{T}}$$

$$= \frac{-b\mathrm{RT}}{(\mathrm{V}-b)^2} + \frac{2\psi}{3\mathrm{V}^{5/3}}$$

$$- \frac{1}{\mathrm{V}^{2/3}}\frac{\partial \psi}{\partial p}\left[\frac{-\mathrm{RT}}{(\mathrm{V}-b)^2} + \frac{5\psi}{3\mathrm{V}^{8/3}}\right] \Big/ \left[1 + \frac{\partial \psi}{\partial p}\Big/ \mathrm{V}^{5/3}\right] \quad . \quad (13)$$

from (12).

Hence if $p\mathrm{V}$ has a minimum or stationary value on the isothermal, *i. e.* if $[\partial(p\mathrm{V})/\partial \mathrm{V}]_{\mathrm{T}} = 0$, then

$$\left[\frac{2\psi}{3\mathrm{V}^{5/3}} - \frac{b\mathrm{RT}}{(\mathrm{V}-b)^2}\right]\left[1 + \frac{\partial \psi}{\partial p}\Big/ \mathrm{V}^{5/3}\right]$$

$$= \frac{1}{\mathrm{V}^{2/3}}\frac{\partial \psi}{\partial p}\left[\frac{-\mathrm{RT}}{(\mathrm{V}-b)^2} + \frac{5\psi}{3\mathrm{V}^{8/3}}\right],$$

which reduces to

$$\frac{2\psi}{3\mathrm{V}^{5/3}} - \frac{b\mathrm{RT}}{(\mathrm{V}-b)^2} - \frac{\psi\dfrac{\partial \psi}{\partial p}}{\mathrm{V}^{10/3}} + \frac{\mathrm{RT}\dfrac{\partial \psi}{\partial p}}{(\mathrm{V}-b)\mathrm{V}^{5/3}} = 0. \quad . \quad (14)$$

If T be supposed to be eliminated between (11 *a*) and (14) we get the state path for the p, V diagram on which lie all minimum values of $p\mathrm{V}$ for the different isothermals. In general, the limiting value of $p\mathrm{V}$ on this path as V is made indefinitely great, i. e. p indefinitely small, need not be finite. But experiment goes to show * that a finite limiting value of $p\mathrm{V}$ under these circumstances does exist, and this fact may be made use of to specify ψ more closely. We make the further assumption that $\psi = p^{\lambda} f(\mathrm{T})$, where λ is to be found, and $f(\mathrm{T})$ is as yet arbitrary.

Under these circumstances, the relation (14), as V is made

* See, *e. g.*, Lewis, *loc. cit.* p. 82.

indefinitely great for a fixed value of T, approaches asymptotically the relation

$$\frac{2}{3b}p^{\lambda}V^{1/3}f(T)-RT-\frac{\lambda p^{2\lambda-1}}{bV^{4/3}}[f(T)]^2+\frac{\lambda RT}{bV^{2/3}}p^{\lambda-1}f(T)=0, \quad . \ . \ . \quad (15)$$

i. e. approaches *

$$\frac{2}{3}\frac{(pV)^{\lambda}f(T)}{bV^{\lambda-1/3}}-RT-\frac{\lambda(pV)^{2\lambda-1}[f(T)]^2}{bV^{2\lambda+1/3}}+\frac{\lambda RT(pV)^{\lambda-1}f(T)}{bV^{\lambda-1/3}}=0. \quad . \ . \ . \quad (15\,a)$$

Since pV is supposed finite under these conditions, we deduce that $\lambda=1/3$, and further that

$$f(T)=6RT\Big/\left[\tfrac{2}{3}(pV)^{1/3}+\frac{RT}{3(pV)^{2/3}}\right]=b(RT)^{2/3}, \quad . \quad (16)$$

under the assumed conditions, viz., $pV\rightarrow RT$.

We may sum up the conclusions of this section by saying that if $\psi(p,T)$ of (11) involves a single power only of p, then considerations of the limiting value of the isothermal pV minima as $V\rightarrow\infty$ indicate that the equation of state is of the form

$$\left[p+\frac{p^{1/3}f(T)}{V^{5/3}}\right](V-b)=RT. \quad . \ . \ . \ . \quad (17)$$

The Nature of $f(T)$.

§ 5. We now assume $f(T)$ to be of the form aT^{μ}, where a and μ are constants, so that $\psi=ap^{1/3}T^{\mu}$.

From (8) and (9), remembering that $V=4b$ and $n=5/3$, we have respectively

$$RT_c=\frac{15}{4^{8/3}}\frac{ap_c^{1/3}T_c^{\mu}}{b^{2/3}}, \quad p_c=RT_c/15b. \quad . \ . \quad (18)$$

Hence, eliminating p_c, we find

$$R^{2/3}T_c{}^{2/3-\mu}=\frac{15^{2/3}a}{4^{8/3}\,b}. \quad . \ . \ . \ . \ . \quad (18\,a)$$

If we denote the limiting temperature referred to in (16) by T_m, and utilize therein the value of $f(T)$, viz. aT^{μ}, we get

$$R^{2/3}T_m{}^{2/3-\mu}=\frac{a}{b}. \quad . \ . \ . \ . \ . \ . \ . \quad (19)$$

* pV is here supposed to remain finite and positive. It will readily be seen that $\lambda=-\frac{1}{6}$ is not permissible in (15), as this would give $pV=RT/4$, whereas we ought to have $pV=RT$. There is a third possibility, viz.: $\lambda-\frac{1}{3}=2\lambda+\frac{1}{3}$, *i. e.* $\lambda=-\frac{2}{3}$. This leads to $f(T)/(pV)^{5/3}=RT/pV-1$, *i. e.* to $f(T)=0$, which does not help us.

Comparing (18 *a*) and (19) we find

$$\left(\frac{T_m}{T_c}\right)^{1-3\mu/2} = \frac{256}{15}. \quad . \quad . \quad . \quad . \quad . \quad (20)$$

The probable mean limiting value of T_m/T_c from experiment is *circa* 3. Introducing this value in (20) we find $\mu = -1{\cdot}055$. The author proposes to replace this by the value minus unity. In this case, (20) shows that the derived value of T_m/T_c is 3·11, a value which is not very far from observed experimental results*. It may be noted that on van der Waals' equation, the ratio T_n/T_c is 3·375, whilst Dieterici's equation requires some modification to enable a proper value of T_m to be deduced.

The results of this section enable us to complete our equations (2), (11), and (17) in the form

$$\left[p + \frac{ap^{1/3}}{TV^{5/3}}\right](V-b) = RT. \quad . \quad . \quad . \quad . \quad (21)$$

Reduced Equation of State.

§ 6. Corresponding to the equation of state (21), we have from (18) and (18 *a*)

$$R^{2/3}T_c^{5/3} = \frac{15^{2/3}a}{4^{8/3}b}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

$$p_c^5 = R^3a^3/(15)^3(4b)^8. \quad . \quad . \quad . \quad . \quad (23)$$

If π, ν, and θ be the *reduced* pressure, volume, and temperature respectively, *i. e.* the pressure, volume, and absolute temperature respectively each expressed in terms of its critical value, we have from (21)

$$\left[\pi + \frac{\pi^{1/3}}{\theta\nu^{5/3}} \frac{a}{p_c^{2/3}V_c^{5/3}T_c}\right]\left(\nu - \frac{b}{V_c}\right) = \theta \cdot \frac{RT_c}{p_cV_c}.$$

Remembering that $V_c = 4b$, and that $RT_c/p_cV_c = 15/4$, we find after a little reduction the reduced equation of state in the simple form

$$\left[\pi + \frac{4(\pi\nu)^{1/3}}{\theta\nu^2}\right]\left(\nu - \frac{1}{4}\right) = \frac{15\theta}{4} \quad . \quad . \quad . \quad . \quad (24)$$

This may be compared with the reduced equation of van der Waals, viz.

$$\left(\pi + \frac{3}{\nu^2}\right)\left(\nu - \frac{1}{3}\right) = \frac{8\theta}{3}. \quad . \quad . \quad . \quad . \quad (25)$$

The presence of the θ term in the manner indicated on the

* See, *e. g.*, Lewis, *loc. cit.* p. 82.

left-hand side of (24) is analogous to a similar presence in the equation of Clausius *. On comparing the π correction terms of (24) and (25), it will be noticed that, in the author's proposed equation, the term $4(\pi\nu)^{1/3}/\theta$ replaces the numerical quantity 3 in (25). The other differences between (24) and (25) are numerical.

It need hardly be said that the nature of (14) implies the existence of what is sometimes called the principle of corresponding states.

State Path for Isothermal $\pi\nu$ Minima.

§ 7. We proceed to discuss more fully the conditions under which the product pV is a minimum on an isothermal, and to do this we shall use the reduced variables π, ν, and θ.

If we write (24) in the form

$$\pi\nu = \frac{15\theta\nu}{4\nu-1} - \frac{4(\pi\nu)^{1/3}}{\theta\nu},$$

we easily see that

$$\left[\frac{d(\pi\nu)}{d\nu}\right]_\theta = \frac{-15\theta}{(4\nu-1)^2} + \frac{4(\pi\nu)^{1/3}}{\theta\nu^2} - \frac{4(\pi\nu)^{-2/3}}{3\theta\nu}\left[\frac{d(\pi\nu)}{d\nu}\right]_\theta,$$

from which we infer that when $\pi\nu$ is a minimum on the isothermal θ=constant, *i. e.* when $d(\pi\nu)/d\nu=0$,

$$15\theta^2\nu^2 = 4(\pi\nu)^{1/3}(4\nu-1)^2. \quad . \quad . \quad . \quad . \quad (26)$$

If we make $\nu\longrightarrow\infty$ in this equation (and thereby take $\pi\nu=\frac{15}{4}\theta$), we find $\theta=3{\cdot}11$ in agreement with § 5.

On substituting the value of $(\pi\nu)^{1.3}$ from (26) in (24), we find

$$\theta = \frac{\pi(4\nu-1)^2}{15(4\nu-2)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

Either (26) or (27) may be regarded as specifying the locus of the $\pi\nu$ minima. It is, however, more convenient to express this locus in terms of two variables only, and these are now taken to be π (denoted now by x) and $\pi\nu$ (denoted by y).

If we eliminate θ between (24) and (27), we find † after some reduction

$$240[4y^2-4xy+x^2] = y^{5/3}[16y^2-8xy+x^2]. \quad . \quad (28)$$

* θ similarly occurs in the equation of D. Berthelot.

† Ignoring the factor $(4y-x)$ which cancels out.

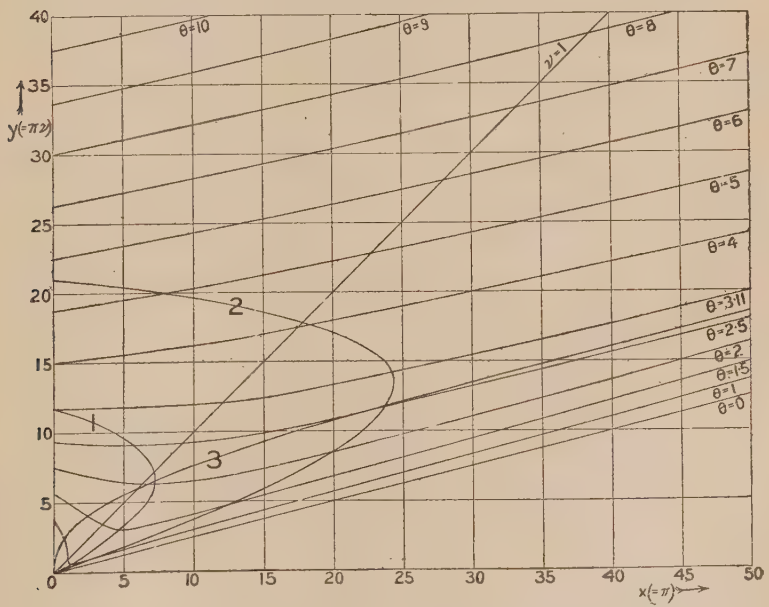
This equation can be solved as a quadratic in x, and we thus obtain

$$x=4y[120-y^{5/3}\pm\sqrt{60y^{5/3}}]/[240-y^{5/3}]. \quad . \quad (29)$$

It may be verified that for x and y both positive, and $\theta>0$ (under which circumstances $y>x/4$), the ambiguous sign is to be taken as negative, and (29) reduces to

$$x=4y[2\sqrt{15}-y^{5/6}]/[4\sqrt{15}-y^{5/6}]. \quad . \quad . \quad . \quad (30)$$

If the positive sign be taken for the ambiguous case of (29) we should get the negative signs of (30) replaced by positive signs. The curve so obtained and running continuously from the origin would have $x=4y$ as asymptote. The diagram (in which y is plotted against x for different isothermals) shows that under the given conditions this curve does not correspond to the physically real locus of minimum values of y on the isothermals.



The Curve (1) is $x=4y[2\sqrt{15}-y^{5/6}]/[4\sqrt{15}-y^{5/6}]$.

„ „ (2) is $x=y[32\sqrt{5}y^{1/6}-4\sqrt{2}y]/[11\sqrt{5}y^{1/6}-\sqrt{2}y]$.

„ „ (3) is $60x=y^{5/3}(4y-x)$.

This physically real locus given by (30) is shown in the diagram (Curve 1). It will be noticed that, starting from

the origin, the locus lies above the line $x=4y$, and ultimately x vanishes again when $y^{5/6}=2\sqrt{15}$, *i.e.* when $y=11{\cdot}66$. This corresponds * to $\theta=3{\cdot}11$. For values of y greater than that given by $y^{5/6}=4\sqrt{15}$, *i.e.* for $y>26{\cdot}8$, there is another branch of the curve given by (30). This branch approaches asymptotically $x=4y$, but lies below this line †. It therefore does not correspond to anything physically real.

Referring to the applicable region of (30), we have

$$\frac{dx}{dy}=4-\frac{8\sqrt{15}}{[4\sqrt{15}-y^{5/6}]^2}\cdot\left[4\sqrt{15}-\frac{1}{6}y^{5/6}\right].$$

Hence $dx/dy=0$ when $y^{5/3}-\frac{23}{3}\sqrt{15}\,.\,y^{5/6}+120=0$. Solving this as a quadratic in $y^{5/6}$, we find $6y^{5/6}=38{\cdot}5\sqrt{15}$ or $7{\cdot}5\sqrt{15}$ ‡. The former of these values corresponds to the branch of (30) lying below the line $x=4y$. The latter value (which gives $y=6{\cdot}63$) corresponds to a real state of the fluid, and gives $x=7{\cdot}23$, $\theta=2{\cdot}06$. The state point thus obtained is that corresponding to the greatest value of x ($=\pi$) on the locus of isothermal $\pi\nu$ minima.

Joule-Thomson Inversion Curve.

§ 8. In connexion with the well-known porous-plug experiment, we have as the condition for the vanishing of the Joule-Thomson effect,

$$\theta\left(\frac{\partial\nu}{\partial\theta}\right)_\pi-\nu=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

From (24) we find

$$\frac{\partial\nu}{\partial\theta}=\left[\frac{15}{4}+\frac{(4\nu-1)(\pi\nu)^{1/3}}{\theta^2\nu^2}\right]\Big/\left[\pi+\frac{4(\pi\nu)^{1/3}}{\theta\nu^2}-\frac{5(4\nu-1)(\pi\nu)^{1/3}}{3\theta\nu^3}\right];$$

hence from (31) the inversion curve satisfies

$$\pi\nu+\frac{8(\pi\nu)^{1/3}}{3\theta\nu^2}-\frac{20(\pi\nu)^{1/3}}{3\theta\nu}=\frac{15}{4}\theta. \quad . \quad . \quad (32)$$

But from (24)

$$\pi\nu+\frac{4(\pi\nu)^{1/3}}{\theta\nu}-\frac{\pi}{4}-\frac{(\pi\nu)^{1/3}}{\theta\nu^2}=\frac{15}{4}\theta. \quad . \quad . \quad . \quad (33)$$

* When $x=0$, $\theta=4y/15$. This point is sometimes called the Boyle point.

† For then $x>4y$.

‡ Approximately.

On equating the left-hand sides of (32) and (33) we find

$$\theta = \frac{4(\pi v)^{1/3}}{3\pi}\left[\frac{32}{v} - \frac{11}{v^2}\right]. \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

Substituting this value of θ in (24) we find

$$\left[\pi + \frac{3\pi}{32v-11}\right]\left(v - \frac{1}{4}\right) = \frac{5(\pi v)^{1/3}}{\pi}\left[\frac{32}{v} - \frac{11}{v^2}\right],$$

or in terms of the variables x and y,

$$\sqrt{2}y(4y-x) = \pm\sqrt{5}y^{1/6}(32y-11x), \quad . \quad (35)$$

which may also be written

$$x = \frac{y[32\sqrt{5}y^{1/6} \pm 4\sqrt{2}y]}{11\sqrt{5}y^{1/6} \pm \sqrt{2}y} \quad . \quad (36)$$

If the ambiguous signs in this result be taken as positive, then the ambiguous sign in (35) is to be taken negative. In this case, since physically $4y > x$, it follows that $32y < 11x$, and hence from (34) θ is negative. Thus negative signs are to be taken in (36).

The inversion curve (36) (with negative signs) is shown in the diagram (Curve 2). It will be seen that the curve closely resembles a parabola, and cuts the axis of y both at the origin and at $y^{5/6} = 8\sqrt{2}\cdot 5$, *i. e.* at $y = 21\cdot 0$, which corresponds to $\theta = 5\cdot 6$. In the immediate neighbourhood of the origin, x/y tends to the value $32/11$ as y diminishes, and under these circumstances an application of (24) shows that θ^2 tends to the value $512y^{1/3}/605$, and hence θ tends to zero. In this connexion it may be noted that this temperature-limit (of absolute zero) is different from the lower of the limits arising in the cases of inversion with van der Waals' or Dieterici's equations of state.

The maximum value of π on the physically real portion of (36) may be obtained by putting $dx/dy = 0$. We find

$$\frac{dx}{dy} = 4 - \frac{12\sqrt{5}[11\sqrt{5} - \frac{1}{6}\sqrt{2}y^{5/6}]}{[11\sqrt{5} - \sqrt{2}y^{5/6}]^2},$$

and equating this to zero we obtain

$$4y^{5/3} - 43\sqrt{10}y^{5/6} + 880 = 0,$$

or

$$(4y^{5/6} - 11\sqrt{10})(y^{5/6} - 8\sqrt{10}) = 0. \quad . \quad . \quad . \quad (37)$$

The diagram shows that the proper value to be taken is given by $y^{5/6} = 11\sqrt{10}/4$, i. e. $y = 13\cdot 41$, which corresponds to $x = 24\cdot 38$ and $\theta = 2\cdot 84$. In perusing the inversion curve on

the diagram given, it is to be remembered that the ordinates y only measure θ for the case of $x\ (=\pi)=0$.

Variation of Specific Heat at Constant Volume with Volume.

§ 9. We proceed to investigate the variation of K_V (the specific heat at constant volume) with volume, using the well-known result

$$\left(\frac{\partial K_V}{\partial V}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V . \quad . \quad . \quad . \quad . \quad (38)$$

We shall employ the critical values of pressure, volume, and absolute temperature as units, and write (38) in the form

$$\left(\frac{\partial K_\nu}{\partial \nu}\right)_\theta = \theta\left(\frac{\partial^2 \pi}{\partial \theta^2}\right)_\nu , \quad . \quad . \quad . \quad . \quad (38a)$$

where K_ν denotes the specific heat at constant volume measured as the amount of heat required to raise unit mass through a temperature range equal to the critical temperature, the heat being measured in work units with the unit of work equal to the product of the critical pressure and the critical volume.

We readily find that

$$\frac{\partial \pi}{\partial \theta}\left[1+\frac{4(\pi\nu)^{1/3}}{3\theta\pi\nu^2}\right] = \frac{15}{4\nu-1}+\frac{4(\pi\nu)^{1/3}}{\theta^2\nu^2}, \quad . \quad . \quad (39)$$

from (24), and after further differentiation and reduction

$$\frac{\partial^2 \pi}{\partial \theta^2} = 120(\pi\nu)^{1/3}(\alpha^2-\alpha-1)/\theta^3\nu^2(2+\alpha)^3, \quad . \quad . \quad (40)$$

where $\alpha = 15\theta/\pi(4\nu-1)$. Thus $\dfrac{\partial^2 \pi}{\partial \theta^2}$ and $\left(\dfrac{\partial K_\nu}{\partial \nu}\right)_\theta$ vanish when

$$\alpha^2-\alpha-1=0,$$

or for real physical conditions when $\alpha=(\sqrt{5}+1)/2$. In this case

$$\frac{15\theta}{\pi(4\nu-1)} = \frac{\sqrt{5}+1}{2}, \quad . \quad . \quad . \quad . \quad . \quad (41)$$

which from (24) can be written as

$$\frac{4(\pi\nu)^{1/3}}{\theta\nu^2} = \frac{\pi}{2}(\sqrt{5}-1). \quad . \quad . \quad . \quad . \quad (42)$$

Eliminating θ from (41) and (42) we obtain

$$60(\pi\nu)^{1/3}/\pi^2\nu^2(4\nu-1)=1,$$

or

$$60x = y^{5/3}(4y-x). \quad . \quad . \quad . \quad . \quad . \quad (43)$$

This curve is shown in the diagram (Curve 3). It cuts the line $\nu=1$ near the isothermal $\theta=2$. We deduce that K_ν is stationary near the critical volume when θ is in the neighbourhood of 2. In this connexion, it may be observed that variations of K_ν with volume giving rise to a maximum value near the critical volume have actually been noted *, as also have analogous variations of $\left(\frac{\partial^2 p}{\partial T^2}\right)_\nu$.

From (40) it follows that $\left(\frac{\partial K_\nu}{\partial \nu}\right)_\theta$ is positive when $\alpha^2-\alpha-1$ is positive, *i. e.* when $\alpha>(\sqrt{5}+1)/2$. Further consideration shows that this is the case when $60x>y^{5/3}(4y-x)$, that is when x has values greater than those corresponding to (43). Thus to the right of the curve (43) as shown in the diagram, K_ν increases with ν, whilst to the left of the curve the opposite is the case. The curve (43) therefore corresponds to *maximum* values of K_ν.

The variation of K_p with p at constant temperature can be treated using the equation $\left(\frac{\partial K_p}{\partial p}\right)_T=-T\left(\frac{\partial^2 V}{\partial T^2}\right)_p$, but the algebraic details are somewhat laborious. It is sufficient to note that $\left(\frac{\partial K_p}{\partial p}\right)_T$ can theoretically become infinite. It will be found that this is the case when

$$\frac{\theta^2}{(4\nu-1)^2}-\frac{(\pi\nu)^{1/3}}{9\nu^3}=0, \quad . \quad . \quad . \quad . \quad (44)$$

in which case both $\left(\frac{\partial\theta}{\partial\nu}\right)_\pi$ and $\left(\frac{\partial\pi}{\partial\nu}\right)_\theta$ vanish. The curve (44) is thus merely the locus of points of maximum or minimum pressure on the isothermals, and clearly passes through the point which represents the critical state. In view of the fact (see below) that points of maximum or minimum pressure on the isothermals do not correspond to stable conditions, the curve (44) has only theoretical interest.

Further Details.

§ 10. We shall give here a few further points concerning (24). We can write this in the form

$$\pi+\frac{4\pi^{1/3}}{\theta\nu^{5/3}}=\frac{15\theta}{(4\nu-1)}, \quad . \quad . \quad . \quad . \quad . \quad (45)$$

which for given values of ν and θ is a cubic in $\pi^{1/3}$. There

* See Kuenen, *loc. cit.* p. 118; also H. Kammerlingh Onnes and W. H. Keesom, *loc. cit.* p. 142.

will always be one real value of $\pi^{1/3}$ satisfying (45), and since

$$\left[\frac{-15\theta}{2(4\nu-1)}\right]^2+\left[\frac{4}{3\theta\nu^{5/3}}\right]^3>0,$$

for positive values of ν and θ, there will be one real value only under these circumstances *.

We can also write (24) in the form

$$f(\nu^{1/3})\equiv\nu^{3/3}-\frac{1}{4}\left(\frac{15\theta}{\pi}+1\right)\nu^{5/3}+\frac{4}{\theta\pi^{2/3}}\nu^{3/3}-\frac{1}{\theta\pi^{2/3}}=0, \quad . \quad (46)$$

which for given values of π and θ is an equation of the eighth degree in $\nu^{1/3}$. Since the pairs of successive terms involving $\nu^{7/3}$, $\nu^{6/3}$ and $\nu^{2/3}$, $\nu^{1/3}$ are absent from (46), it follows † that in general at least four of the roots are imaginary. For positive values of π and θ we have the following scheme :—

$\nu=$	$-4^{3/5}/\theta^{3/5}\pi^{2/5}$	$1/4$	$\left(\frac{15\theta}{\pi}+1\right)\Big/4$
$f=$	+	−	+

Thus there are always two real values of ν satisfying (46) under these circumstances, one lying between $\frac{1}{4}$ and $\left(\frac{15}{\pi}+1\right)\Big/4$, the other lying between $-4^{3/5}/\theta^{3/5}\pi^{2/5}$ and $\frac{1}{4}$. Of these, of course, only the former corresponds to a real physical state. We have thus accounted for six of the roots of (46). A plotting of a few isothermals on a π,ν diagram shows that the remaining two roots are either both real or both imaginary. For positive values of π, ν, and θ, the isothermals so drawn resemble in many ways the curves obtained with van der Waals' equation, *i.e.* for $\theta<1$, a constant pressure-line under certain circumstances will cut an isothermal in three physically real points. For values of $\theta>1$, a constant pressure line will cut an isothermal in only one point for which $\nu>1/4$.

For values of $\theta<1$, the effect of evaporation at constant pressure and temperature is represented on the π,ν diagram in the usual way by drawing a line at constant pressure π to cut the appropriate isothermal in such a way that the two

* From the general theory of Cardan's solution of the cubic.

† De Gua's Rule. See, *e.g.*, Burnside and Panton, 'Theory of Equations' (1886 ed.), p. 180.

areas bounded by the line and the isothermal are numerically equal. The saturation-curve can then be constructed from a series of such evaporation-lines. A simple analytical expression for the saturation-curve does not appear feasible *.

It is convenient to represent the various results arising from (24) by means of a diagram in which $\pi\nu$ is plotted against ν, and this has been done in the diagram appended. The arithmetical work involved can be done conveniently by taking (for a given isothermal) different values of $y\ (=\pi\nu)$ and solving the various quadratic equations which arise for $x\ (=\pi)$. The results so obtained can be utilized for determining ν if required for a π, ν diagram.

Lastly, we may note that (24) can be expressed as

$$\nu - \frac{1}{4} = \frac{15\theta}{4\pi[1+4(\pi\nu)^{1/3}/\theta\pi\nu^2]} = \frac{15\theta}{4\pi} - \frac{15(\pi\nu)^{1/3}}{\pi^2\nu^2} + \text{etc.}, \quad . \quad . \quad . \quad (47)$$

provided $\theta\nu(\pi\nu)^{2/3} > 4$. Under these circumstances, for large values of ν we shall have approximately

$$\nu - \frac{1}{4} = \frac{15\theta}{4\pi} - \frac{4^{5/3}}{15^{2/3}\theta^{5/3}}, \quad . \quad . \quad . \quad . \quad (48)$$

which may, *e.g.*, be compared with Callendar's equation for steam †.

Conclusion.

§ 11. The author has been led in the present paper to put forward (21) and its equivalent form (24) as a new equation of state. The chief properties of a fluid which follow this equation are as follows:

(1) For large specific volumes V, the fluid tends to follow the perfect gas law.

(2) For high pressures and low temperatures, V tends to a fixed volume b, which is taken to represent the volume of the fluid in the liquid state.

(3) The isothermals closely resemble those obtained following van der Waals' equation. Critical phenomena are indicated, and at the critical point $V = 4b$, whilst $RT/pV = 15/4$.

(4) Below a certain temperature ($3{\cdot}11T_c$), along each isothermal the product pV first falls and then rises with

* This is true, of course, even for the simpler van der Waals' equation.

† Corresponding to the last term of (48), Callendar has a term involving $1/\theta^{10/3}$. For the region to which Callendar's equation is applicable, the steam is too much of a vapour to allow of a strict comparison with (48).

continued increase of pressure. The greatest pressure for which a minimum value of pV on an isothermal occurs is $7{\cdot}23p_c$, the corresponding temperature being $2{\cdot}06T_c$.

(5) Inversion in the porous-plug experiment is indicated, but this can only take place if the temperature is below $5{\cdot}6T_c$. The greatest pressure which will allow of inversion is $24{\cdot}36p_c$, the corresponding temperature being $2{\cdot}825T_c$.

(6) The specific heat K_v at constant volume is found to vary with the volume (with the temperature constant). As the volume increases from a small value, K_v at first rises, attains a maximum value, and then diminishes. For temperatures in the neighbourhood of $2T_c$, the specific volume giving the maximum value of K_v is about the critical volume.

The chief difficulty in giving the proposed equation of state more than an empirical status lies in the fact that the pressure-correction term ϕ of (2) involves p as well as V and T.

XXXV. *A Tentative Theory of Light Quanta.*

By Louis de Broglie *.

I. *The Light Quantum.*

THE experimental evidence accumulated in recent years seems to be quite conclusive in favour of the actual reality of light quanta. The photoelectric effect, which is the chief mechanism of energy exchange between radiation and matter, seems with increasing probability to be always governed by Einstein's photoelectric law. Experiments on the photographic actions, the recent results of A. H. Compton on the change in wave-length of scattered X-rays, would be very difficult to explain without using the notion of the light quantum. On the theoretical side Bohr's theory, which is supported by so many experimental proofs, is grounded on the postulate that atoms can only emit or absorb radiant energy of frequency ν by finite amounts equal to $h\nu$, and Einstein's theory of energy fluctuations in the black radiation leads us necessarily to the same ideas.

I shall in the present paper assume the real existence of light quanta, and try to see how it would be possible to reconcile with it the strong experimental evidence on which was based the wave theory.

For the sake of simplicity, it is a very natural assumption to admit that all light quanta are identical and that only

* Communicated by R. H. Fowler, M.A.

their velocities are different. We shall then assume that the "mass at rest" of every light quantum has a given value m_0: since the atoms of light have velocities very nearly equal to the Einstein's limiting velocity c, they must have an extremely small mass (not infinitely small in a mathematical sense); the frequency of the corresponding radiation must be related to the whole energy of a quantum by the relation

$$h\nu = \frac{m_0 c^2}{\sqrt{1-\beta^2}}, \quad \left(\beta = \frac{v}{c}\right);$$

but, since $1-\beta^2$ is very small, we can write

$$\beta = \frac{v}{c} = 1 - \frac{1}{2}\frac{m_0^2 c^4}{h^2\nu^2}.$$

The light quanta would have velocities of slightly different values, but such that they cannot be discriminated from c by any experimental means. It then seems that m_0 should be at most of the order of 10^{-50} gr.

Naturally, the light quantum must have an internal binary symmetry corresponding to the symmetry of an electromagnetic wave and defined by some axis of polarization. We shall refer again later to this remark.

II. *The Black Radiation as a Gas of Light Quanta.*

Let us consider a gas made up by the light quanta we have described above. At a given temperature (not too near to the absolute zero) almost all these atoms of light would have velocities $v=\beta c$ very nearly equal to c. The whole energy of one of these atoms is

$$\mathrm{W} = \frac{m_0 c^2}{\sqrt{1-\beta^2}},$$

and its momentum is

$$\mathrm{G} = \frac{m_0 v}{\sqrt{1-\beta^2}};$$

so we have approximately

$$\mathrm{G} = \frac{\mathrm{W}}{c}.$$

The pressure of such a gas on the walls of the enclosure is easily seen to be

$$p = \frac{n}{6} \cdot 2\mathrm{G}c = \tfrac{1}{3} n\mathrm{W},$$

if n is the number of light quanta in an element of volume.

This expression is the same as the one given by the electromagnetic theory, whilst without using the Relativity formulæ we should have found a result twice as great as this.

Now the question arises, Can we use for the quanta gas Maxwell's energy partition law? In Einstein's dynamics, Liouville's theorem, on which is based all Statistical Dynamics, is still valid; we can then use for the elementary cell of extension-in-phase a value proportional to $dx\,dy\,dz\,dp\,dq\,dr$, if x, y, z are rectangular coordinates and p, q, r the corresponding momenta. In consequence of the canonical distribution law, the number of atoms whose representative points are in the element $dx\,dy\,dz\,dp\,dq\,dr$ must be proportional to

$$e^{-\frac{W}{kT}}dx\,dy\,dz\,dp\,dq\,dr = e^{-\frac{W}{T}}.4\pi G^2\,dG\,dv,$$

if dv is the element of volume and G the momentum. But, since $G=\frac{W}{c}$, this number is also given by

$$C' \times e^{-\frac{W}{kT}} w^2\,dw\,dv.$$

Each quantum has a total energy $h\nu$; then the whole energy contained in the volume dv and carried by light quanta of energy $h\nu$ is

$$C' e^{-\frac{h\nu}{kT}} \nu^3\,d\nu\,dv.$$

This is obviously Wien's limiting form of the radiation law. Two years ago * I was able to show that, by using the hypotheses made by Planck that the element of extension in phase was $\frac{1}{h_3}dx\,dy\,dz\,dp\,dq\,dr$, it was possible to find for the radiant energy density the value

$$u_\nu\,d\nu = \frac{8\pi h}{c^3}\nu^3\,e^{-\frac{h\nu}{kT}}d\nu.$$

This was an encouraging result, but not quite complete. The assumption of finite elements of extension in phase seemed to have a somewhat arbitrary and mysterious character. Moreover, Wien's law is only a limiting form of the actual radiation law, and I was obliged to suppose some kind of quanta aggregation for explaining the other terms of the series.

It seems that these difficulties are now removed, but we shall first of all explain many other ideas; we shall later on return to the "black radiation" gas.

* See *Journal de Physique*, November 1922.

III. *An important Theorem on the Motion of Bodies.*

Let us consider a moving body whose "mass at rest" is m_0; it moves with regard to a given observer with velocity $v=\beta c$ $(\beta<1)$. In consequence of the principle of energy inertia, it must contain an internal energy equal to m_0c^2. Moreover, the quantum relation suggests the ascription of this internal energy to a periodical phenomenon whose frequency is $\nu_0=\frac{1}{h}m_0c^2$. For the fixed observer, the whole energy is $\frac{m_0c^2}{\sqrt{1-\beta^2}}$ and the corresponding frequency is $\nu=\frac{1}{h}\frac{m_0c^2}{\sqrt{1-\beta^2}}$.

But if the fixed observer is looking at the internal periodical phenomenon, he will see its frequency lowered and equal to $\nu_1=\nu_0\sqrt{1-\beta^2}$, that is to say this phenomenon seems for him to vary as $\sin 2\pi\nu_1 t$. The frequency ν_1 is widely different from the frequency ν; but they are related by an important theorem which gives us the physical interpretation of ν.

Let us suppose that, at time 0, the moving body coincides in space with a wave whose frequency ν has the value given above and which spreads with velocity $\frac{c}{\beta}=\frac{c^2}{v}$. This wave, however, cannot carry energy, according to Einstein's ideas.

Our theorem is the following:—"*If, at the beginning, the internal phenomenon of the moving body is in phase with the wave, this harmony of phase will always persist.*" In fact, at time t, the moving body is at a distance from the origin $x=vt$ and its internal phenomenon is proportional to $\sin 2\pi\nu_1\frac{x}{v}$; at the same place the wave is given by $\sin 2\pi\nu\left(t-\frac{\beta x}{c}\right)=\sin 2\pi\nu x\left(\frac{1}{v}-\frac{\beta}{c}\right)$. The two sines will be equal; the harmony of phase will again occur if the following condition is realized:

$$\nu_1=\nu(1-\beta^2),$$

a condition clearly satisfied by the definitions of ν and ν_1.

This important result is implicitly contained in Lorentz's time transformation. If τ is the local time of an observer carried along with the moving body, he will define the

internal phenomenon by the function $\sin 2\pi\nu_0\tau$. According to Lorentz's transformation, the fixed observer must describe the same phenomenon by the function $\sin 2\pi\nu_0 \frac{1}{\sqrt{1-\beta^2}}\left(t-\frac{\beta x}{c}\right)$, which can be interpreted as the representation of a wave of frequency $\frac{\nu_0}{\sqrt{1-\beta^2}}$ spreading along the x axis with velocity $\frac{c}{\beta}$.

We are then inclined to admit that any moving body may be accompanied by a wave and that it is impossible to disjoin motion of body and propagation of wave.

This idea can also be expressed in another way. A group of waves whose frequencies are very nearly equal has a "group velocity" U, which has been studied by the late Lord Rayleigh, and which in the usual theory is the velocity of "energy propagation." This group velocity is linked with the "phase velocity" V by the relation

$$\frac{1}{U}=\frac{d\left(\frac{\nu}{V}\right)}{d\nu}.$$

If ν is equal to $\frac{1}{h}\frac{m_0c^2}{\sqrt{1-\beta^2}}$ and V to $\frac{c}{\beta}$, we find $U=\beta c$—that is to say, "*The velocity of the moving body is the energy velocity of a group of waves having frequencies* $\nu=\frac{1}{h}\cdot\frac{m_0c^2}{\sqrt{1-\beta^2}}$ *and velocities* $\frac{c}{\beta}$ *corresponding to very slightly different values of* β."

IV. *Dynamics and Geometrical Optics.*

Trying to extend the former ideas to the case of variable velocity is a rather difficult but very suggestive problem. If in any medium a moving body describes a curved path, we say that there is a field of force; at each point the potential energy may be calculated, and the body when crossing this point has a velocity determined by the constant value of its whole energy. Now, it seems natural to suppose that the phase wave must have at any point a velocity and a frequency fixed by the value *which* β *would have if the body were there.* During its propagation the phase wave has a constant frequency ν and a constantly variable velocity V.

Perhaps a new electromagnetism will give us the laws of this complicated propagation, but it seems that we know beforehand the final result : " *The rays of the phase wave are identical with the paths which are dynamically possible.*" In fact, the paths of the rays can be computed as in a medium of variable dispersion by means of Fermat's principle, which may be written here (λ wave-length, ds element of path) :

$$\delta \int \frac{ds}{\lambda} = \delta \int \frac{\nu\, ds}{V} = \delta \int \frac{m_0 \beta c}{\sqrt{1-\beta^2}}\, ds = 0.$$

The principle of least action in its Maupertuisian form gives the dynamical paths by the equation

$$\delta \int m_0 c^2 \left(\frac{1}{\sqrt{1-\beta^2}} - \sqrt{1-\beta^2} \right) dt$$
$$= \delta \int \frac{m_0 \beta^2 c^2}{\sqrt{1-\beta^2}}\, dt = \delta \int \frac{m_0 \beta c}{\sqrt{1-\beta^2}}\, ds = 0,$$

a result which justifies the above statement.

It is now so simple a matter to show that the theorem of phase harmony is always valid that it seems not necessary to develop the proof.

The present theory suggests an interesting explanation of Bohr's stability conditions. At time 0 the electron is in a point A of its trajectory. The phase wave starting at this instant from A will describe all the path and meet again the electron in A'. It seems quite necessary that the phase wave shall find the electron in phase with itself. This is to say : " The motion can only be stable if the phase wave is tuned with the length of the path." The tune relation is then :

$$\int \frac{ds}{\lambda} = \int_0^T \frac{m_0 \beta^2 c^2}{h \sqrt{1-\beta^2}}\, dt = n$$

(n whole number ; T revolution period).

Now, we can write the stability condition of the quantum theory in a general form given by Einstein which degenerates into the manifold Sommerfeld's conditions for quasi-periodical cases in consequence of the infinite number of the pseudo-periods. Let us call $p_x\, p_y\, p_z$ the momenta ; then Einstein's general condition is

$$\int (p_x\, dx + p_y\, dy + p_z\, dz) = nh \quad (n \text{ whole number}),$$

or also

$$\int_0^T \frac{m_0}{\sqrt{1-\beta^2}}(v_x^2+v_y^2+v_z^2)\,dt = \int_0^T \frac{m_0}{\sqrt{1-\beta^2}}\beta^2c^2dt = nh,$$

which is precisely the result obtained above.

V. *The Propagation of Light Quanta and the Coherence Problem.*

We will now make use of our results for studying the propagation of free light quanta whose velocities are always slightly lower than c. We can say: "The atom of light whose whole energy is equal to $h\nu$ is the seat of an internal periodical phenomenon which, for a fixed observer, has at each point of space the same phase as a wave spreading in the same direction with velocity very nearly equal to c (very little greater)." The light quantum is in some manner a part of the wave, but for explaining interferences and other phenomena of the wave optics it is necessary to see how several light quanta can be parts of the *same* wave. This is the coherence problem.

In the light quanta theory, it seems necessary to make the following hypothesis: "When a phase wave crosses an excited atom, this atom has a certain probability of emitting a light quantum determined at each instant by the intensity of the wave." Perhaps this hypothesis will seem arbitary, but I think that any theory of coherence must adopt some postulate of this kind.

The emissions of γ-rays by radioactive substances are known to be quite independent, but this cannot be considered as an objection against our view because the "mean life" of any known radioactive atom is always so much greater than the period of the γ-rays.

Thus when an atom emits a light quantum, a spherical phase wave is simultaneously emitted and, crossing over the neighbouring atoms of the point source, will excite other emissions. The non-material phase wave will carry many little drops of energy which slide slowly upon it and whose internal phenomena are coherent.

VI. *Diffraction by a Screen Edge and the Inertia Principle.*

The corpuscular theory of light meets here a great difficulty. It is known since Newton that the light rays passing within a short distance of a screen edge are no longer straight

but that some penetrate into the geometrical shadow. Newton ascribed this deviation to the action of some forces which would be exerted by the edge upon the light corpuscle. It seems to me that this phenomenon is perhaps worthy of a more general explanation. Since an intimate connexion seems to exist between motion of bodies and propagation of waves, and since the rays of the phase wave may now be considered as the paths (the possible paths) of the energy quanta, we are inclined to give up the inertia principle and to say: "A moving body must always follow the same ray of its phase wave." In the continuous spreading of the wave, the form of the surfaces of equal phase will change continuously and the body will always follow the common perpendicular to two infinitely near surfaces.

When Fermat's principle is no longer valid for computing the ray path, the principle of least action is no longer valid for computing the body path. I think that these ideas may be considered as a kind of synthesis of optics and dynamics.

We must still specify some points. The ray which now assumes in our ideas an important physical significance may be defined as above by the *continuous* spreading of a small part of the phase wave; it cannot be defined at each point by the geometrical sum for all the waves of the vector which is called in electromagnetic theory "radiant or Poynting's vector." Let us consider a sort of Wiener's experiment. We send a train of plane waves on a perfectly reflecting plane mirror in the normal direction; standing waves are set up; the reflecting mirror is a nodal plane for the electric vector, the plane at a distance $\frac{1}{4}\lambda$ from the mirror is a nodal plane for the magnetic vector, the plane at a distance $\frac{1}{2}\lambda$ of the mirror is again a nodal plane for the electric vector, and so on. In each nodal plane the radiant vector is null. May we say that these planes are not crossed by any energy? Evidently not, we can only say that the interference states in these planes are always the same. In every interference case we should find similar intricacies. In the wave theory, the propagation of energy has a somewhat fictitious character, but, in return, the exact calculation of the interference fringes is easily made; we shall try in the next paragraph to see why it is so.

VII. *A new Explanation of Interference Fringes.*

Consider how we can detect the presence of light at a point in space—by direct perception of the scattered light, by photographic tests, by calorific effects, and perhaps by some

other means. It seems that all these means can, in fact, be reduced to photoelectric actions and scattering. Now, when a light quantum crosses a material atom, it has a certain probability of being absorbed or scattered, which can depend on external agencies. If then a theory succeeds in determining these probabilities without taking account of the actual motion of energy, it may be able to predict correctly the average reaction between radiation and matter at each place. Following the electromagnetic theory (and Bohr's correspondence principle is consistent with this view) I have been inclined to suppose that, for a material atom, the probability of absorbing or scattering a light quantum is determined by the geometrical sum of one of the defining vectors of the phase waves crossing upon it. The last hypothesis is, in fact, quite analogous to that which is admitted by electromagnetic theory when it links intensity of disclosable light with the intensity of the resultant electric vector. Thus, in the Wiener's experiment, the photographic action only occurs in the nodal planes of the electric vector; according to the electromagnetic theory, the luminous magnetic energy is not disclosable.

Let us now consider Young's interference experiment. Some atoms of light pass through the holes and diffract along the ray of the neighbouring part of their phase waves. In the space behind the wall, their capacity of photoelectric action will vary from point to point according to the interference state of the two phase waves which have crossed the two holes. We shall then see interference fringes, however small may be the number of diffracted quanta, however feeble may be the incident light intensity. The light quanta do cross all the dark and bright fringes; only their ability to act on matter is constantly changing. This kind of explanation, which seems to remove at the same time the objections against light quanta and against the energy propagation through dark fringes, may be generalized for all interference and diffraction phenomena.

VIII. *The Quanta and the Dynamical Theory of Gases.*

For the sake of calculating the entropy constants and the so-called "chemical constants," Planck and Nernst have been obliged to introduce the quantum idea into the theory of gases. As explained above, Planck chooses an element of extension in phase equal to

$$\frac{1}{h^3}dx\,dy\,dz\,dp\,dq\,dr \quad \text{or} \quad \frac{4\pi}{h^3}m_0^{3/2}\sqrt{2w}\,dw\,dx\,dy\,dz.$$

We shall now try to justify this assumption.

Each atom of velocity βc may be considered as linked with a group of waves whose phase velocity is $V=\frac{c}{\beta}$, frequency $\frac{1}{h}\frac{m_0c^2}{\sqrt{1-\beta^2}}$, and group velocity $U=\beta c$. The state of the gas can only be stable if the waves corresponding to all the atoms make up a system of standing waves. Using a well-known method given by Jeans, we find for the number of waves per unit of volume whose frequencies are included in the interval $\nu, \nu+d\nu$ * :

$$n_\nu d\nu = \frac{4\pi}{UV^2}\nu^2\,d\nu = \frac{4\pi}{c^3}\beta\nu^2\,d\nu.$$

If w is the kinetic energy of an atom and ν the corresponding frequency, then :

$$h\nu = \frac{m_0c^2}{\sqrt{1-\beta^2}} = w + m_0c^2 = m_0c^2(1+\alpha),$$

where $\alpha = \frac{w}{m_0c^2}$.

It is now very easy to find that $n_\nu d\nu$ is given by the equation :

$$n_\nu d\nu = \frac{4\pi}{h^3}m_0^2c(1+\alpha)\sqrt{\alpha(2+\alpha)}\,dw.$$

Each phase wave can carry with it one, two, or more atoms, so that, according to the canonical law, the number of atoms whose energy is $h\,.\,\nu$, will be proportional to :

$$\frac{4\pi}{h^3}m_0^2c(1+\alpha)\sqrt{\alpha(2+\alpha)}\,dw\,dx\,dy\,dz\sum_1^\infty e^{-\frac{nh\nu}{kT}}.$$

Let us first consider a material gas whose atoms have relatively great mass and relatively small velocities. We can then neglect all the terms of the series except the first, and we can also put $1+\alpha=1$. The number of atoms whose kinetic energy is w will be, neglecting a constant factor,

$$\frac{4\pi}{h^3}m_0^{3/2}\sqrt{2w}\,dw\,dx\,dy\,dz\,e^{-\frac{w}{kT}},$$

a result which justifies Planck's method and leads to the usual form of Maxwell's law.

In the case of the light quanta gas α is always great, and, moreover, we must use all the series. In consequence of the

* Léon Brillouin, *Théorie des Quanta*, p. 38. Paris: A. Blanchard.

internal binary symmetry of the light quantum, we must introduce a factor 2, and we find that the radiant energy density is proportional to:

$$\frac{8\pi}{h^3c^3}w^3\sum_1^\infty e^{-\frac{nh\nu}{kT}}dw = \frac{8\pi h}{c^3}\frac{\nu^3}{e^{\frac{h\nu}{kT}}-1}d\nu.$$

A method developed in the *Journal de Physique*, of November 1922, shows that the proportionality factor is unity, so that we obtain the actual radiation law.

IX. *Open Questions.*

The conceptions stated in this paper, if they are received, will necessitate a wide modification of the electromagnetic theory. The so-called "electric and magnetic energies" must be only a kind of average value, all the real energy of the fields being probably of a corpuscular fine-grained structure. The building up of a new electromagnetism seems to be a very difficult task, but we have one directive idea: according to the correspondence principle and to the above statements, the defining vectors of the old electromagnetic theory would give the probability of the reaction between matter and the fine-grained energy.

The new electromagnetism will give the solution of many problems. The laws of propagation of waves given by Maxwell's theory will probably be valid for the energyless light phase waves, and the scattering of the radiant energy will be explained by the resulting curvature of the rays (viz., light quanta paths). There seems to be a great analogy between scattering of radiation and scattering of corpuscles; lowering of particles' velocities by crossing through a screen may also be similar to the lowering of X-ray frequencies by scattering, which recently has been computed and experimentally checked by A. H. Compton.

Explaining optical dispersion will be more difficult. The classical theories (including the electron theory) gives only an average view of this phenomenon, which is produced by complex elementary reactions between radiation and atoms; we shall certainly be obliged here also to distinguish accurately the real motion of energy from the propagation of the resulting interference state. The kind of "resonance" shown by the variations of refractive index seems no longer to be irreconcilable with discontinuity of light.

Many other questions remain open: What is the mechanism

of Bragg's absorption? What occurs when an atom passes from a stable state to another, and how does it eject a single quantum? How may we introduce the granular structure of energy into our conceptions of elastic waves and into Debye's theory of specific heats?

Finally, we must remark that the quantum relation remains still a kind of postulate defining the constant h whose actual significance is not at all cleared up; but it seems that the quantum enigma is now reduced to this unique point.

Summary.

In the present paper it is assumed that the light is essentially made up of light quanta, all having the same extraordinarily small mass. It is shown mathematically that the Lorentz-Einstein transformation joined with the quantum relation leads us necessarily to associate motion of body and propagation of wave, and that this idea gives a physical interpretation of Bohr's analytical stability conditions. Diffraction seems to be consistent with an extension of the Newtonian Dynamics. It is then possible to save both the corpuscular and the undulatory characters of light, and, by means of hypotheses suggested by the electromagnetic theory and the correspondence principle, to give a plausible explanation of coherence and interference fringes. Finally, it is shown why quanta must take a part in the dynamical theory of gases and how Planck's law is the limiting form of Maxwell's law for a light quanta gas.

Many of these ideas may be criticized and perhaps reformed, but it seems that now little doubt should remain of the real existence of light quanta. Moreover, if our opinions are received, as they are grounded on the relativity of time, all the enormous experimental evidence of the "quantum" will turn in favour of Einstein's conceptions.

1 October, 1923.

Note.—Since I have written this paper, I have been able to give to the results contained in the fourth section a somewhat different, but much more general form.

The principle of least action for a material point can be expressed in the space-time notation by the equation :—

$$\delta \int \sum_{1}^{4} J_i \, dx_i = 0,$$

if the J_i are the covariant components of a four-dimensional

vector whose time component is the energy of the point divided by c and space components are the components of its momentum.

Similarly, in studying the propagation of waves, we have to write :—

$$\delta \int \sum_1^4 O_i \, dx^i = 0,$$

if the O_i are the covariant components of a four-dimensional vector whose time component is the frequency divided by c and space components the components of a vector drawn along the ray and equal to $\frac{\nu}{V} = \frac{1}{\lambda}$ (V phase velocity). Now, the quantum relation says that $J_4 = h O_4$. More generally, I suggest putting $\overrightarrow{J} = h \overrightarrow{O}$. From this statement, the identity of the two principles of Fermat and Maupertius follows immediately, and it is possible to deduce rigorously the velocity of the phase wave in any electromagnetic field.

XXXVI. *The Kinetic Energy of Electrons emitted from a Hot Tungsten Filament in an Atmosphere of* (a) *Argon*, (b) *Hydrogen*. *By* J. F. Congdon, *B.Sc.*, *A.Inst.P.*, *King's College, London* *.

RECENT experiments by J. H. Jones †, L. H. Germer ‡, and H. H. Potter § have shown conclusively that the electrons emitted from hot metals *in vacuo* possess kinetic energy in accordance with Maxwell's distribution law.

This paper deals with experiments on the kinetic energy of the electrons emitted from a hot tungsten filament in (*a*) an atmosphere of argon, (*b*) an atmosphere of hydrogen.

The kinetic energy of the electrons emitted from hot platinum in hydrogen has been measured by Mr. H. H. Potter, who found that for pressures of the gas greater than 50×10^{-3} mm., the slopes of the curves obtained by plotting the logarithms of the thermionic currents against the corresponding applied retarding voltages were less than

* Communicated by Prof. O. W. Richardson, F.R.S.
† Proc. Roy. Soc. vol. cii. p. 734 (1923).
‡ Science, vol. lvii. p. 392 (1923).
§ Phil. Mag. vol. xlvi. p. 768 (Nov. 1923).

in vacuo, but that in every case the linear relation required by Maxwell's law held.

The apparatus used in the experiments described here was similar to that used by H. H. Potter, and for a description reference should be made to his paper.

The method of measuring the kinetic energy of the electrons was that used by J. H. Jones in the latter part of his work.

Temperature of the Filament.

It was not necessary to know the temperatures of the filament in these experiments, but it was found useful to determine them in order to test the accuracy of the experiment by a comparison of the slopes of the curves obtained *in vacuo* with the theoretical values. The resistances of the filament at room temperatures and high temperatures were calculated from the condition of the balance of the Wheatstone bridge ; and the temperature of the hot filament was estimated from its change in resistance by means of data given by Langmuir * for tungsten. The introduction of gas into the tube reduced the resistance of the hot filament, but did not affect that of the cold filament appreciably. Therefore to keep the hot filament at the same temperature as *in vacuo*, it was only necessary to increase the heating current until a balance of the Wheatstone bridge was restored and the resistance of the filament had the same value as *in vacuo*.

It was usually found that the initial electron emission was not uniform. This was probably due to some compound which formed on the surface of the filament during the process of cooling. Prolonged heating (about two hours) of the filament in a high vacuum at a high temperature, however, got rid of this effect, and the emission gradually assumed a constant value. It was therefore necessary to heat the filament in a high vacuum until the emission was constant before taking a set of observations, after a filament had been allowed to cool.

The argon used in these experiments was prepared commercially and supplied in cylinders by the British Oxygen Co. It contained an appreciable quantity of oxygen and nitrogen, and therefore had to be purified before being admitted into the thermionic tube. This was done by passing it over small pieces of heated calcium contained in three small porcelain boats inside a long unglazed silicon tube

* Phys. Rev. vol. vii. no. 3 (March 1916).

which was heated by surrounding it with a small electric furnace. Calcium only absorbs oxygen and nitrogen when they are present in small quantities, so it was not always possible to obtain argon entirely free from oxygen when the pressure of argon was comparatively large, *e. g.* 1 cm.; and filaments fused quickly if oxygen were present to any extent. A comparatively pure sample at a high pressure was obtained eventually, and thermionic currents in argon at a pressure of 5·5 cm. were obtained.

The purity of the argon was tested by examining its spectrum produced in a small vacuum discharge-tube. This, however, is not a very delicate test, since oxygen and nitrogen may be present in small quantities without being detected spectroscopically.

The hydrogen used was obtained by heating a palladium tube connected to the apparatus. The gas obtained in this way was very pure and free from oxygen, with the result that no fusing of filaments took place.

The method of experiment was to obtain a current-potential curve at a constant temperature of the filament in high vacuum (about 1×10^{-6} mm. pressure), and then repeat the curve with various pressures of gas in the thermionic tube at the same temperature of the filament.

The currents in high vacua were all measured with the pumps working.

Since the value of $\log i/i_0$ is independent of the units in which the current is measured, the current in all the curves is expressed in terms of the galvanometer deflexion.

The linear relation between $\log i/i_0$ and V only holds for low values of the current, and since at these retarding voltages it is only a small fraction of the saturation current, the observations were difficult to take and were liable to big percentage error unless the saturation currents had high values.

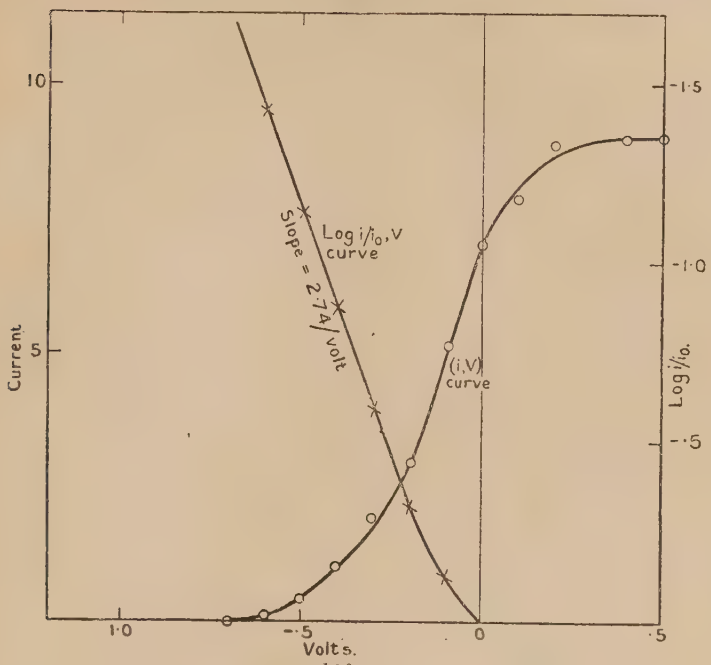
Results of Observations.—(*a*) Argon.

Experiment 1.—Length of filament = 3·5 cm., diameter = 0·005 cm. The tube was heated in the furnace for about two hours and the filament, during cooling, glowed for about two hours until the thermionic emission was constant.

Temperature of filament = 1650° K.

Three curves similar to fig. 1 were obtained, showing the relation between the current and the applied potential.

Fig. 1.



Pressure of Argon $= \frac{120}{1000}$ mm. Temp. $= 1650°$ K.

The following results were obtained :—

Pressure of Argon.	Slope of (log i/i_0, V) Curve.
0 mm.	2·76
183×10^{-3} „	2·90
120×10^{-3} „	2·74

Theoretical slope in vacuum $= 2·85$.

Experiment 2.—A new filament of the same dimensions as that used in Experiment 1.

Tube heated in electric furnace for one hour and the filament afterwards glowed for about two hours.

Temperature of filament $= 1500°$ K.

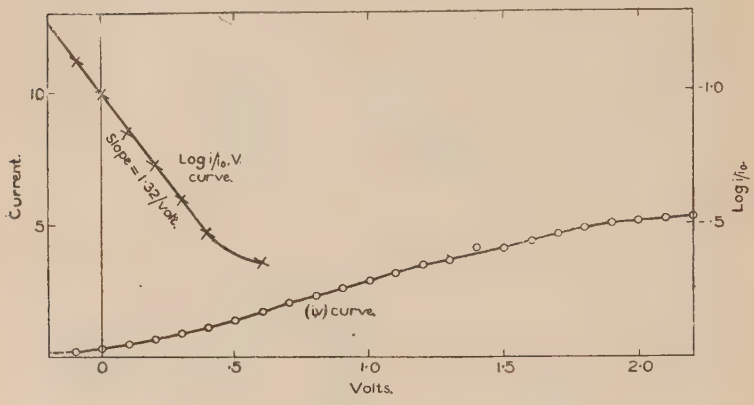
Two current-potential curves were obtained and gave the following results :—

Pressure of Argon.	Slope of (log i/i_0, V) Curve.
0 mm.	2·95
140×10^{-3} „	2·94

Theoretical slope in vacuum $= 3·14$.

Experiment 3.—The same filament as used in Experiment 2. *Temperature of filament* = 1800° K.

Fig. 2.



Pressure of Argon = 4·5 cm. Temp. = 1800° K.

Ten curves were obtained and gave the following results :—

Pressure of Argon.	Slope of (log i/i_0, V) Curve.
0 mm.	2·51
240×10^{-3} ,,	2·455
150×10^{-3} ,,	2·71
100×10^{-3} ,,	2·48
70×10^{-3} ,,	2·55
0 ,,	2·50
2·0 cm.	2·60
3·0 ,,	2·62
4·5 ,,	1·32
5·5 ,,	1·75

Theoretical slope = 2·55.

(*b*) Hydrogen.

Experiment 4.—The copper cylinder used in the previous experiments was thoroughly cleaned and the tungsten filament replaced by another having the same dimensions.

The tube and cylinder were heated for about $2\frac{1}{2}$ hours in the electric furnace, and the filament glowed for about two hours in a high vacuum.

Temperature of filament = 1900° K.

Five curves were obtained and gave the following results :—

Pressure of Hydrogen.	Slope of (log i/i_0, V) Curve.
0×10^{-3} mm.	2·39
150×10^{-3} „	1·65
80×10^{-3} „	1·44
125×10^{-3} „	1·586
185×10^{-3}	2·085

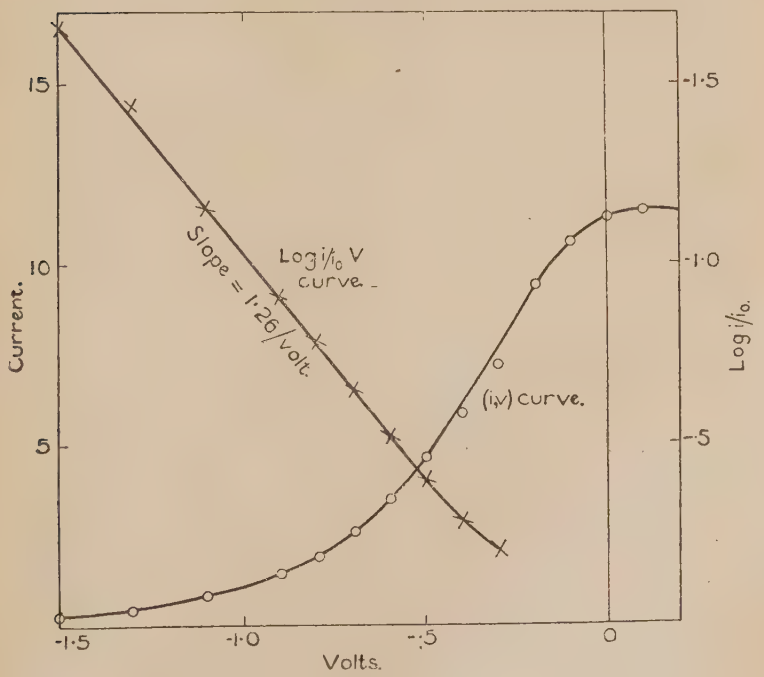
Theoretical slope = 2·45.

Experiment 5.—A new filament was used having the same dimensions as the previous one.

The copper cylinder was quite clean, so it was not necessary to heat in the electric furnace. The filament was glowed for about two hours in a high vacuum.

Temperature of filament = 1600° K.

Fig. 3.



Pressure of Hydrogen = $\frac{250}{1000}$ mm. Temp. = 1600° K.

Seven curves were obtained and gave the following results :—

Pressure $\times 10^{-3}$ mm.	Slope of ($\log i/i_0$, V) Curve.
0	2·96
235	1·99
80	1·78
135	2·25
175	2·86
110	2·27
250	1·26

Theoretical slope = 2·94.

Discussion of Results.

The slopes of ($\log i/i_0$, V) curves have been obtained for electrons emitted from a hot tungsten filament in high vacuum, and give results in close agreement with those demanded by Maxwell's distribution law.

The slopes of the curves have also been obtained in pressures of argon ranging from 70×10^{-3} mm. to 50 mm. The results clearly indicate that up to a pressure of 3 cm. the linear relation is maintained and the slopes have the same values as *in vacuo*. At pressures of argon of 4·5 cm. and above the linear relation still holds, but the slopes are much less than those for the corresponding temperature obtained *in vacuo*. The reason for this sudden drop in slope is not clear. It is hardly possible that it is due to an increase in the energy of the electrons ; but it may be due to local fields at the surface of the filament. Impurities in the gas may also account in some way for the change in slope.

The curves for hydrogen give quite different results. In nearly every case the slopes of the ($\log i/i_0$, V) curves have values which are considerably lower than those for the corresponding temperature obtained *in vacuo*. The linear relation, however, has been found to hold for low values of the current.

The slope of the curves does not in any way appear to be a function of the pressure of the hydrogen, although the results of Experiment 4 seem to indicate that the slope increases with increasing pressure. This conclusion, however, is not confirmed by the results of Experiment 5, in which the slopes bear no relation at all to the pressure of the hydrogen. For example, the slope at a pressure of 110×10^{-3} mm. is 2·27, and for a pressure of 250×10^{-3} mm. it is 1·26.

The change seems to depend somewhat on the previous

treatment of the filament. With curves obtained immediately after admitting the hydrogen, the slope was usually much less than that obtained *in vacuo* ; but if the cold filament were allowed to remain in the gas for any length of time before taking the curve, the slope tended towards the normal value. Further investigation of this point, however, is necessary before arriving at a definite conclusion.

The general results obtained in hydrogen agree closely with those obtained by Mr. Potter for platinum in hydrogen.

The low slopes obtained in hydrogen are not satisfactorily accounted for. They cannot in any way be due to the pressure of the gas and the consequent decrease in the length of the mean free path, as in that case the same effect on the slope would be expected in argon and some definite relation would exist between the slope and the pressure of the gas ; but the slopes in argon are the same as *in vacuo* and are unaffected by the pressure of the gas.

They may arise on account of local fields at the surface of the filament, but since the current-potential curves saturate easily in hydrogen, this view is not readily supported. Prof. Richardson has made the suggestions (1) that owing to the pressure of hydrogen the surface of the filament is in a state of polarization, and that consequently the electrons are emitted with a velocity above the normal ; (2) that the electrons may start with a Maxwell distribution which is subsequently modified by local fields, thus giving rise to abnormal measured values.

In any case hydrogen has some peculiar property not possessed by argon.

Conclusions.

(1) The average energy of the electrons emitted from a hot tungsten filment *in vacuo* is in close agreement with the requirements of Maxwell's distribution law.

(2) The presence of argon over a wide range of pressures has no effect on the measured average energy.

(3) The presence of hydrogen, even at low pressures, appears to increase the measured average energy considerably whilst maintaining the linear relation of the ($\log i/i_0$, V) curve.

I wish to thank Prof. O. W. Richardson for suggesting this research and for his advice and interest during the course of the experiments.

XXXVII. *On Soft X-Rays from Carbon.* (Preliminary communication.) *By* P. I. Lukirsky, *Lecturer in Physics, Petrograd University* *.

THE filling of the gap between short ultra-violet and soft Röntgen rays presents some interest in addition to the effect of obtaining a continuous scale of electromagnetic waves. The determination of the characteristic wave-lengths of the lightest elements—and it is precisely these waves which lie in the above gap—is of great importance in the question of atomic structure, for the laws of atomic dynamics must take a particularly simple form with respect to the light elements containing a relatively small number of electrons. For instance, in the case of carbon, which has been the object of our investigation, each atom contains but six electrons, of which two form the K-group and four the L-group, coinciding with the optical one. The extreme ultra-violet spectrum of carbon has been recently investigated by Millikan, who succeeded by means of his diffraction grating in extending it to 202 Å and later to 136 Å.

On the other hand, soft X-rays have been measured by the crystal method up to wave-lengths of 12 Å. In order to measure wave-lengths within the interval 12–136 Å, we may avail ourselves of the photo-electric action, *i. e.* of the secondary cathode rays streaming from a metal surface illuminated by X-rays. This was the principle of the method used in the experiments of Richardson, Kurth, Hughes, McLennan, and Holtsmark. These authors measured the total photo-electric current due to X-rays of a given substance, or rather a given anti-cathode bombarded by primary cathode rays of gradually increasing speed.

When the energy of these primary electrons (*i. e.* the voltage applied) is small, the anti-cathode emits a continuous Röntgen spectrum only, whose intensity gradually increases along with the voltage, causing a corresponding increase of the secondary current. When the energy of the primary electrons is large enough to excite the emission of characteristic rays, the rate of increase must abruptly change, which will be manifested by a break on the curve: secondary current-voltage. In this way the limiting energy of eV (V, voltage; e, electronic charge) of the K and L series of various light elements has been determined, and from it the

* Communicated by the Author.

limiting frequency ν deduced by means of the quantum relation

$$h\nu = e\mathrm{V},$$

where h is Planck's constant.

The above method does not permit the direct determination of the wave-length of the characteristic lines *emitted* by the substance considered. Besides, when the energy of the primary electrons but slightly exceeds the limiting energy of an X-ray series, the characteristic spectrum, as well known, is very weak. Therefore, the exact position of the break cannot be determined accurately, as is clearly seen from the great divergence of the results obtained by various authors for the same series under apparently identical conditions.

It is well known that the maximum velocity of secondary electrons generated by ordinary, ultra-violet, and Röntgen rays is given by Einstein's relation

$$\tfrac{1}{2}mv^2 = h\nu - p_1 - p_2,$$

where m is the mass, v the velocity of the electrons, ν the frequency of rays, p_1 and p_2 the work done by an electron in escaping from the atom and getting through the surface layer of the metal (p_2 corresponds to the contact potential). If the electrons are generated by monochromatic rays, they must be composed of distinct groups with perfectly definite velocities corresponding to different atomic levels—that is, to different values of the work p_1. Measuring in some way or another the velocity of the electrons and taking account of the work p_1 and p_2, we can determine the frequency ν.

The velocity of the secondary electrons can be measured by deflecting them in a given magnetic field. In this method, however, out of the whole mass of electrons streaming from the metal we must take a very narrow pencil; therefore, in the case of light elements, where the total intensity of the secondary current is very small, we can hardly expect to find a measurable effect in this way.

The method of a longitudinal electric field, stopping the electrons which stream from the illuminated plate of a plane condenser, is also inapplicable. If these electrons had the same velocity directed at random with respect to the plate, they would be stopped to a different amount depending upon the normal component of the velocity, the component parallel to the plate, *i. e.* perpendicular to the field, being unaffected by the latter. This corresponds to a parabolic shape of the curve secondary current-stopping potential.

In case of several different velocities we should get a composite curve, which it is practically impossible to analyse into the component parabolas, and thus draw any information about the corresponding groups of secondary electrons.

These shortcomings of the electrostatic method can be easily avoided if, instead of a *plane* condenser, usually adopted in experiments of this kind, we take a *spherical* one. When the inner sphere is illuminated by the rays of frequency ν, it emits secondary electrons in different directions but with the same initial velocities v. In radial electric field the electrons will move along any curve of second order and will reach the outer sphere as they move away from perihelion. When the retarding potential $e\mathrm{V}$ reaches the value nearly equal to their initial energy, only then will the electrons all at once be stopped and driven back to the inside sphere (this may be easily shown using the equations of motion of the electron in radial field). Therefore, electrons of the same group, that is of the same initial velocity, will be stopped at the same time that the potential difference exceeds the critical value V, determined by the relation $\mathrm{V}e=\frac{1}{2}mv^2$. This will correspond to a very marked drop of the secondary current on the curve current-potential.

I have used this method to determine the velocities of the secondary electrons. A similar method was used by Richardson and Compton for measurements of velocities of photoelectrons*. They illuminated by ultra-violet light the centre of a small *plate* placed inside the sphere. Then all electrons starting from the centre of the sphere moved approximately against the lines of force, and all were stopped by the field in spite of the difference in direction of their initial velocities. The advantage of the use of a *spherical condenser* consists in the fact that in this case it is not necessary to have a very small illuminated area. This is essential in the case of illumination by X-rays, which we cannot bring to a focus. For instance, if the radii of the sphere are in the ratio of 1 : 10 and the retarding potential $e\mathrm{V}$ is equal to 0·99 of the kinetic energy of the electrons, then all the electrons with the initial velocity of any direction *still reach* the outer sphere. With further increase of field the current begins to drop. For the ratio of the radii 1 : 5 the current begins to drop when the retarding potential has reached the value $e\mathrm{V}=0{\cdot}96\times\frac{1}{2}mv^2$.

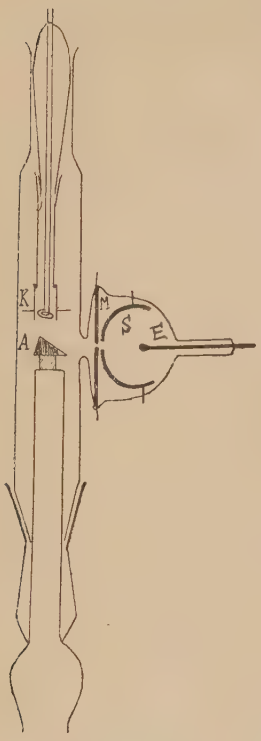
From these data it is easily seen that the illuminated inside sphere may have a comparatively great surface.

The apparatus is represented in fig. 1. The anticathode

* See Phil. Mag. October 1912.

A contained a bit of diamond which was bombarded by a pencil of (primary) cathode rays from a Coolidge cathode K.

Fig. 1.



The primary potential difference varied from 250 to 750 volts and the primary current from 30 to 80 milliamperes. X-rays from carbon (diamond) passed through a lead diaphragm M, and further through a hole in the external sphere, or rather hemisphere, S, falling on a thin zinc sphere E connected with a string electrometer. I measured the intensity of the secondary current i for different values of the (stopping) potential difference V between E and S. As the intensity of the primary current I was not quite constant, i was always replaced by the ratio $\frac{i}{I}$. The results obtained with a primary potential difference of 750 volts are represented in fig. 2, the stopping potential V being taken as abscissa and the ratio $\frac{i}{I}$ as ordinate. This curve shows three distinct drops: (1) a small one for V = 20–26 volts; (2) another, also very small, for V = 115–123 volts; and (3) a relatively strong drop for V = 248–252 volts. This shows that among the secondary electrons excited by the Röntgen rays there are three distinct groups with perfectly definite velocities, corresponding to the above values of the stopping potential and wholly independent of the energy of the primary electrons. Whence we may conclude that, besides the continuous spectrum exciting secondary electrons of all the possible velocities (up to the limiting one corresponding to 750 volts), the diamond emits a characteristic radiation which is the cause of the electrons with definite velocities.

The numerical values obtained for these velocities may be interpreted as follows:—

Electrons with velocities corresponding to 243–252 volts are due to the K-*line of carbon* ejecting both outer and free electrons from zinc. The energy of one quantum of

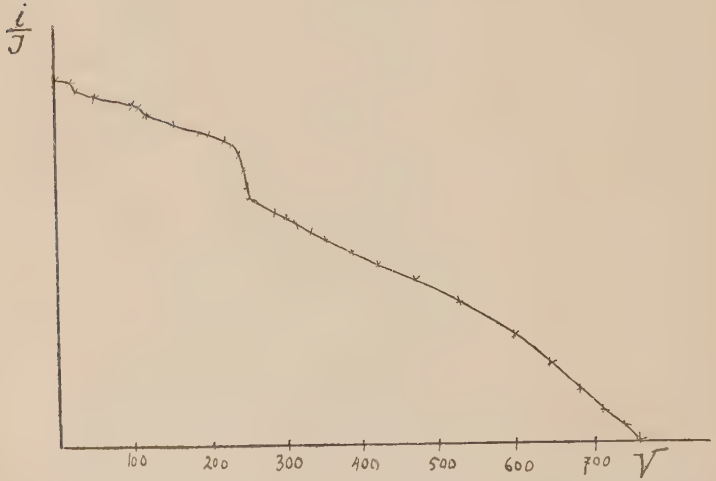
these rays is equivalent to 252 volts + the contact potential of zinc (1–2 volts), which corresponds to a wave-length $\lambda = 48{\cdot}9$ Å. This result is certainly correct with respect to the order of magnitude ; if we take Kurth's numbers for the limits of the K and L series of carbon (289 and 32·9 volts), then for the energy of the K-line we get

$$K = K_g - L_g = 289 - 32{\cdot}9 = 256 \text{ volts.}$$

Richardson gives for $K_g = 286$ volts, what makes $K = 253$ volts, which almost exactly coincides with the above value.

The two other drops of the curve (fig. 2) may be explained in the following way :—The drop corresponding to 110–130

Fig. 2.



volts is due either to the ejection of electrons from the M group of zinc by the K-line of carbon, or of the free and outer electrons by the M-line of the same metal, which must be present as a line of fluorescence. Both explanations are correct with respect to the order of magnitude. Lastly, the small drop corresponding to 20–26 volts must be due to the ejection of electrons by extreme ultra-violet rays of carbon (the line 360 Å, found by Millikan, corresponds to 27–28 volts).

Thus, measuring the velocities of the secondary electrons by means of a stopping electric field of spherical (radial) symmetry, it was possible to determine the wave-length of the carbon K-line, which proves to be 48·9 Å. Although this method gives an accuracy to 1 per cent. only, it seems yet the only one which is used at present for the determination of wave-lengths in the interval considered.

The work is being continued.

Petrograd, September 1923.

XXXVIII. *Notices respecting New Books.*

Relativity. A Systematic Treatment of Einstein's Theory. By J. Rice, M.A., Senior Lecturer in Physics in the University of Liverpool. Pp. xv+397. London: Longmans, Green, & Co. 1923. Price 18*s.* net.)

THE theory of relativity has revolutionized the mental attitude of the physicist towards many of the concepts which he had been taught from his early days, and which have been used in the past as foundation stones upon which the grand structure of physical science has been reared. The question now arises as to what course should be adopted in instructing the coming generation of physicists. Should they be taught the old views until they have graduated and then be compelled at some subsequent time to readjust their point of view? Should they be allowed to study mathematics and physics with the belief at the back of their minds that the new knowledge has dealt a death-blow to all that they are supposed to be learning?

It is such questions as these which the author suggests in his preface. He believes that the young student should make as early an acquaintanceship as possible with the theory, so that he may know exactly to what extent the principles of physical science have been modified by the theory. This volume is therefore written primarily for the science undergraduate to enable him to adapt his mind to the new ideas as he pursues the normal University Courses.

This explains the order in which the subject is here treated, an order which corresponds neither to that usually adopted in works on the subject nor to the historical order of development. After a general introduction, in which the paradoxes into which the older views may lead us are considered, and in which the concepts of space, time, simultaneity, &c. are discussed, the modifications in kinematics and dynamics required by the theory are discussed. This is followed by a discussion from the relativity viewpoint of Maxwell's equations, introducing the Lorentz transformations and Minkowski's concept of a "space-time." A systematic treatment of tensor analysis follows, and this is used for the formulation of differential equations of the electromagnetic field and of the dynamics of continuous media which are compatible with the restricted theory of relativity.

The second part of the book deals with the generalized theory, the principle of equivalence, and the law of gravitation. The necessary extensions in the tensor analysis required for these developments are deduced. In the third part the notion of parallel displacement is introduced, and an account given of the extensions of Einstein's theory by Weyl and Eddington, with a view to deriving a mathematical theory of the electromagnetic field as well as of gravitation. The speculations of de Sitter and Einstein with regard to the finiteness of the Universe are also discussed.

The author has drawn largely upon the works of Weyl and Eddington, and there are no novel features in the mathematical exposition which call for comment. More use might with advantage have been made of the tensor-densities, employed extensively by Weyl. Care has been taken to point out any traps in the analysis into which the unwary may easily fall.

Whilst to those who are familiar with the relativity conceptions the order of treatment followed by Weyl and Eddington is to be preferred, the author is to be commended for this attempt to develop the theory in a manner which can be assimilated by the student along with his other studies. The treatment is carried further than would be necessary for a degree examination, but it is desirable that the discussion of the deductions from the theory should be complete. The student will thus be able, if necessary, to pursue the subject further in his post-graduate studies.

A Treatise on the Theory of Bessel Functions. By G. N. Watson, Sc.D., F.R.S. (Cambridge University Press. 804 pages. Price 70*s.* net.)

Bessel, Neumann, and other related functions investigated in this volume have generally arisen from the solutions of problems in astronomy and physics. Hitherto many of the methods employed may be said to be lacking in rigour, but to the mathematical physicist this want has in no way invalidated the formulæ and numerical results required for the problems in question.

"However important it may be to maintain a uniformly high standard in pure mathematics, the physicist may occasionally do well to rest content with arguments which are fairly satisfactory and conclusive from his point of view."

By his contributions to the theory of Bessel functions, many of which are incorporated in this volume, the author has added considerably to the literature of this subject. He has at the same time given a wealth of results, which are of practical application in physical problems and in the construction of tables of these functions. Of especial importance in this connexion are the chapters on the zeros of Bessel functions, Bessel functions of large order, and Neumann and Kapteyn Series.

The formula for the smallest zero of the Bessel function of high order ν may be compared with that given independently by Emde, viz.:

$$x_1 = \nu + 1{\cdot}8568\,\nu^{\frac{1}{3}} + 1{\cdot}149\,\nu^{-\frac{1}{3}}.$$

Similar series for the first ten zeros have been computed and employed in the calculation of tables similar to those of Bourget.

For functions of nearly equal order and argument, Prof. J. W. Nicholson's formula, involving $J_{\pm\frac{1}{3}}$, is

$$J_\nu(x) \sim \frac{1}{3}\left(\frac{2\alpha}{x}\right)^{\frac{1}{2}}\left\{J_{-\frac{1}{3}} + J_{\frac{1}{3}}\right\},$$

a being written for $x-\nu$, and the argument of $J_{\pm\frac{1}{3}}$, $\frac{1}{3}(2a)^{\frac{3}{2}}/x^{\frac{1}{2}}$. The author has discovered similar expressions for $J_\nu(x)$ and $Y_\nu(x)$, with an upper limit less than $24/\nu$ for the errors involved, from a consideration of the work of Debye. In this, as in so many other examples, the actual errors are considerably less than those indicated above.

In the study of this subject some confusion has arisen from the introduction of a variety of Bessel functions of the second kind. Prof. Watson rightly upholds the view that Weber's function $Y_n(x)$ should be regarded as the standard function of this type.

Not the least valuable feature of the volume is the extensive collection of tables of Bessel functions, with the detailed chapter on their tabulation; tables of the J, Y, H, I, and K functions of zero and unit order, with J, Y, and H of order $\frac{1}{3}$; J functions of higher integral and half odd integral order, with Fresnel's integrals; functions of equal order and argument and the first forty zeros of J_n and Y_n. In the bibliography the author has considerably supplemented that of Nielsen in his *Cylinderfunktionen*.

These brief references convey a very inadequate idea of the contents of this volume, which includes all the more important advances made in recent years. Previous to the publication of this work, many of the most valuable contributions could only be found in scientific and mathematical journals and in the proceedings and transactions of Societies. Prof. Watson has succeeded in keeping pace with the rapid growth of Bessel function literature, and students of both pure and applied mathematics have cause to be grateful to him for devoting an immense amount of labour in making these theoretical and practical results conveniently accessible.

His treatise will long remain the standard work of reference on Bessel functions, and worthily maintains the high traditions of excellence of the Cambridge University Mathematical Series.

An Introduction to the Study of Alternating Currents.
By Dr. A. E. Clayton. (Longmans. 10*s.* 6*d.* net.)

Dr. Clayton has undertaken the task of writing a textbook suitable for the electrical engineer whose mathematical equipment is not too extensive. The work before us can only be commended very strongly, as being fully in accord with the author's purpose. He avoids, at one and the same time, the temptation to overload the subject with long proofs of an analytical nature and the more insidious temptation, to an engineer, to accept somewhat loose reasoning by analogy as equivalent to real demonstration. We are not able to find any omission from the work which calls for attention, and the author has been singularly successful in incorporating into his scheme all the fundamental ideas which are

really vital to the student. We can give the work unqualified commendation, with the suggestion that it should find a place in the electrical library of every college of engineering.

It is, on the whole, conspicuously free from errors, and the publishers may be congratulated on the manner in which it has been produced.

The Atom and the Bohr Theory of its Structure. By H. A. Kramers and H. Holst. (London: Gyldendal. 10*s.* 6*d.* net.)

This work should find a good audience. The mathematical theory underlying current views of atomic structure is entirely suppressed, and the authors professedly set out to give an account of the actual facts known concerning the atom, and the various speculations now in existence, made at the School of Physics which Prof. Bohr has founded in so remarkable a manner at Copenhagen. We regard the existence of this school as being perhaps the second great achievement of Prof. Bohr.

Perhaps it is not possible, in a work of this kind, to make it quite clear to the reader which of the necessarily dogmatic statements are statements of fact, and which are quotations from current speculation, and we must not chide the writers of an excellent work for leaving the reader so often in the position of being unable to decide. A developing theory must contain much pure speculative matter to which no mathematical analysis can yet be applied, and the Bohr theory at the present day is notably one of this type. The writers are themselves very effective members of the school, full of enthusiasm, and able to write in a vivid style. Sometimes a curious note appears, which seems to imply that the theory has made a hard fight for acceptance, and we get a mental picture of Prof. Bohr with his back to the wall, repelling all assaults. This surely does not correspond to history, for the instantaneous general acceptance of the theory was, in fact, a very remarkable and unusual event.

Sir Ernest Rutherford contributes a foreword to the volume, which should be in the library of all those who are interested to know the precise position of thought in the great Danish School of Atomic Theory.

The Theory of Experimental Electricity. By W. C. D. Whetham. (Cambridge University Press, 1923. 12*s.* 6*d.* net.) Third Edition.

The first two editions of this work were excellent, and did not leave much scope for alterations, except those called for by the development of electrical research in new directions. Such alterations as were necessary, however, have been made, and there are considerable additions. The author does not intend to give any comprehensive survey of the vast domain of electrical science as it exists to-day, with all its adjuncts such as the structure of atoms, theory of spectra, and so forth. He has wisely confined himself to the original scheme of the first edition, which was to incorporate the substance of a set of lectures into a per-

manent record of the fundamental principles underlying the usual electrical measurements made in the laboratory by the University student reading for Honours in Physics. The subjects thus treated comprise electrostatics, magnetism, the electric current and induction of currents, thermo-electricity and electrolysis, electric waves, conduction through gases, and radioactivity.

The treatment is lucid and the book is very pleasant to read, and this edition, like its predecessors, will certainly find its way into most electrical laboratories and libraries. As regards its form, we only recall that it is a member of the Cambridge Physical Series.

Clerk Maxwell's Electromagnetic Theory (The Rede Lecture for 1923). By H. A. Lorentz. (Cambridge University Press, 1923. 1*s.* 6*d.* net.)

Prof. Lorentz has paid a fine compliment to English physics by choosing, as the subject of his Rede lecture, the work of James Clerk Maxwell. Lorentz and Larmor developed the work of Maxwell, in its extension to moving media, to the point where it became clear that Maxwell's equations were invariant for uniform motion of the axes of reference. They did not, it is true, apply the simple alternative postulate of Einstein—that no effect of the earth's motion must be looked for,—but they provided the inspiration and analysis which rendered it possible to make this, their deduction, the actual starting-point. Prof. Lorentz sees Maxwell as the pioneer. His account of his work is sympathetic and of profound insight. Prof. Lorentz is well-known, and even loved among English physicists, for his gifts of humour and of understanding, which cannot hide the spark which fired the torch of all recent progress in electron theory and relativity theory. We can only congratulate the University of Cambridge on its choice of a Rede Lecturer and Prof. Lorentz on his lecture.

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. By Dr. J. W. Mellor. (Longmans, Green & Co.) Vol. III., 63*s.* net; Vol. IV,, 63*s.* net.

Vol. III.—The author in this volume takes up the chemistry of Copper, Silver, Gold, and the Alkaline earths. The monumental character of the work is fully maintained: it is very difficult to find any piece of exact knowledge or interesting speculation which is not referred to with an appropriate reference. The author's historical references excite our admiration—for example, the history of Copper begins with Tubal Cain, 3870 B.C., Job, and Deuteronomy. The earliest specimen of bronze from Medûm is chronicled as of date 3700 B.C., with its composition as percentages of tin, copper, and arsenic.

These serve only as examples of the thoroughness of the work. It is almost impossible, in a reasonable time, to count the number of references to the literature of any single element dealt with, or to estimate the amount of research into sources of information which the present account has demanded. The author sets a

model which all future encyclopædias will find a difficulty in imitating. But this feature continues: we dismiss the element Copper, and come upon a similar literature of all its known compounds. Then we turn to Silver, and so on.

In fact, this work is undoubtedly the indispensable reference book for every chemical library. Like the earlier volumes, in a sense, it certainly is; but as the work grows, the author's sense of thoroughness seems to grow with it. The author writes as a chemist, but it is certainly difficult to find any phenomenon of interest to a physicist, who is not also a chemist, which does not receive an adequate mention and discussion. Not even a book of tables is likely to be necessary to the possessor of these volumes, whether he be a physicist, chemist, or engineer. Even the spectroscopist can find the leading wave-lengths of the absorption bands. The whole work is a monumental record of observation and chemical theory, and seems to displace the whole literature of the subject, as at present known in scattered publications in various languages.

Vol. IV.—This volume deals with Radium and Actinium families, Beryllium, Magnesium, Zinc, Cadmium, and Mercury. The treatment is equally exhaustive, and begins with a chapter, of a general kind, on the structure of matter, and the various physical phenomena which have contributed to its elucidation. The second chapter takes up the general question of radio-activity, and gives a very satisfactory account of the chain of products from Radium to Lead. There follows a chapter on the general architecture of the atom, and then the author settles down once more to the more chemical side of his subject, with the whole literature of Beryllium.

Dr. Mellor is doing, for Chemistry, a task which no author has ever even attempted to do for any other branch of science, except perhaps Kayser, in his Handbook of Spectroscopy. But this is on a scale altogether different, as is the subject-matter itself. The manner in which it is being done is beyond criticism, except that perhaps it should not be called a treatise, but an encyclopædia. While we wish the author all possible speed with the succeeding volumes, we may well wonder whether his task can ever reach its end in the lifetime of one man.

Bibliographical History of Electricity and Magnetism, chronologically arranged. By Dr. P. F. Mottelay. (Charles Griffin & Co., Ltd., 1922. 42*s*. net.)

This work is described as an account of researches into the domain of the early sciences, especially from the period of the revival of scholasticism, with biographical and other accounts of the most distinguished natural philosophers throughout the middle ages. In actual fact, the author's claim, here made, is a very modest one, for the work contains much more, and is a worthy memorial of a lifetime spent in collating all available information from unexpected and quite new sources. The sad death of the author just at the close of his work is referred to in a touching

manner by Sir Richard Glazebrook in a foreword he has written for the volume, which was originally dedicated to Lord Kelvin.

The account begins at B.C. 2637, when the Emperor of China used a compass to direct his troops, and ends with Faraday in 1821. We have all quotations from the early Greeks, even Homer, which can bear on a possible knowledge of the compass—every known detail regarding the magnet and the views held concerning it.

The most exhaustive tests a reviewer can make seem to show that nothing is omitted.

The late Prof. Silvanus Thompson writes an introduction, commending the work not only for what it contains, but for the spirit which permeates every page—the spirit of appreciation of the work of those early pioneers who have created the subject as it exists to-day. To find just what any author has ever had to say about Electricity or Magnetism, it is only necessary to refer to these pages. Priority questions can be settled out of hand, with the assurance that the last word has been said.

We can only commend the work very strongly as an indispensable work of reference for any library designed to help either the worker or the student of the literature dealing with electrical science. The publishers are to be congratulated on its form.

Advanced Practical Physics for Students. By B. L. Worsnop and H. J. Flint. (Methuen. 21*s.* net.)

The subject-matter of this work, regarded as an effective laboratory course for Students for Honours in the Universities, is in many respects ideal, and constitutes a great improvement on the courses which are contained in most existing works. The suggested experiments do appear to be suitable for stimulating the imagination of the student, and for giving him a vivid feeling of progress. They can only have been designed, in the sequence here presented, by those who have the essentials of teaching at heart.

While the work can be recommended with confidence, we may perhaps remark that the authors have not always been careful enough to avoid expressions of a slipshod nature, and even modes of statement which defy the ordinary rules of English grammar. Such errors can easily be corrected in a later edition, and seem to imply a somewhat hurried revision of the proofs. We wish the work every success, and a consequent early appearance in a form which is more pleasing to the æsthetic sense which physicists, like others, have.

Méthodes de calcul différentiel et leurs applications. By M. M. G. Ricci and T. Levi-Civita. (Paris: Librairie Scientifique A. Blanchard, 1923. 9 francs.)

This memoir meets a need which is much felt in English mathematics. At one time it appeared in the *Mathematische Annalen*. The present volume is a somewhat tardy reprint, in French. In a real sense, it forms the ultimate basis of

the mathematical developments of Einstein's theory. It is now a matter of common knowledge that Prof. Levi-Civita is one of the outstanding authorities on tensor geometry, whose work so long escaped recognition.

We do not enter into detail regarding the contents of this small volume. They are expressed in the concise and elegant form to which the French language so readily lends itself. The work deserves complete commendation, and, if only as a page in the history of more recent developments, should be on the shelves of every library of physics or of differential geometry.

The Structure of the Atom. By Dr. N. R. Campbell.

(Cambridge University Press. 10*s.* net.)

This work is another of the supplementary chapters to the author's treatise on modern Electrical Theory, and is to be regarded as Chapter XVII. of that Treatise. The author's object is to help students who have taken the usual courses and are now in a position to get into touch with research. This work, like the other supplementary chapters, will fulfil that need by raising all the problems in which progress is now being made in regard to atomic structure, and by indicating the kind of method of attack which will most probably be successful in each instance.

At the same time, it is not possible to say that the very great standard of excellence of the original Treatise has been maintained. Signs of careless writing are numerous, and the MS. has clearly not been sufficiently revised in some places. The author is clearly aware that errors may exist, and apologizes for them with an explanation of the real difficulty which exists in constructing a connected story grouped about a few fundamental conceptions.

The author also refers to the difficulty of ascribing the names of original authors to particular facts or theorems elucidated by many workers, and raises a claim for more prominence of earlier authors who laid the foundations of the structure which Rutherford and Bohr have raised. While agreeing with him, we would point out that he has not applied the principle sufficiently fully. Authors of more recent date whom one naturally looks for are not always referred to at all, even when unquestionably the originators. This is equivalent to saying that the author has not always used the best sources for his information, and has tended to restrict himself to the writings, for example, of Sommerfeld, Bohr, and others, who, while contributing much, have naturally worked on special lines. Much important work by several writers in this Magazine, in the Proceedings of the Royal Society, and elsewhere, has more claim to attention than some of the highly speculative work included.

But we must not emphasize these points, for the author expresses his difficulty in obtaining collaborators who were able to help. He has produced a very readable account in a vivid style. What we have referred to as careless writing could easily be corrected in a new edition, which should be called for in due course.

XXXIX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

Continued from p. 256.

December 5th, 1923.—Proc. A. C. Seward, Sc.D., F.R.S., President and, afterwards, Dr. G. T. Prior, F.R.S., F.G.S., in the Chair.

THE following communications were read:—

1. 'The Geology of the Northern Border of Dartmoor, between Whiddon Down and Butterdon Down.' By Charles William Osman, M.Inst.C.E., F.G.S.

The Lower Carboniferous rocks between the above points, a distance of about 4½ miles, are described, and it is shown that these rocks may (as in the Okehampton border-district) be divided into a Lower Aluminous and a Calcareous Series, and that in this district the Lower Aluminous Series may be subdivided into two zones: the Lower, characterized by the abundance of pyrites; and above this, a zone in which chiastolite is found. The Calcareous Series commences with grey shales above the Lower Aluminous Series, without any physical feature, and contains a volcanic band, generally in a fragmentary condition, mixed with ash, slate, and other fragments, and impregnated with chert; but, at East Underdown, the rock is more solid, and consists of perthitic orthoclase-phenocrysts in a ground-mass of tufted albite-oligoclase, and is a quartzless keratophyre. The author endeavours to show that the corresponding mixed igneous rocks of the North-Western Dartmoor border, which have been variously described as 'trappean rocks', 'metamorphosed tuffs and trachytes', and 'dark igneous rocks', are altered keratophyres.

Above the volcanic band are two limestone-areas: one on the west, near Whiddon Down, and, separated by quartzose rocks, another limestone-area at Drewsteignton. The eastern ends of both these areas are cut by faults with crush, and show a limuritic change of contact-alteration; while the area east of Drewsteignton shows a secondary crush and shearing, producing a hornblendic alteration imposed on the limuritic one. Throughout the length of border considered, the top of the Calcareous Series is formed of grey shales, with hard rock-bands which pass upwards into the Upper Aluminous Series.

The granite south of the Carboniferous border-rocks shows three separate intrusions. These are all from the same magma, but there are sufficient differences to separate them. The first, or great intrusion, is the country-rock granite G, with large orthoclase-phenocrysts measuring up to 7 inches in length, and disseminated tourmaline in the coarse ground-mass: this is generally much decomposed and crushed. The second intrusion, or G 1 granite, broke up the country-rock (G) granite, and occurs as large dykes, and sills overlying the G granite. It has fewer and smaller orthoclase-phenocrysts, larger plagioclase-crystals, and may be

described as a cordierite-biotite-granite. The third, or fine granite (G 2) intrusion, occurs not only in smaller veins and sills, but also in a large marginal intrusion along a width of border of about $2\frac{1}{2}$ miles. This granite overlies both the G and G 1 granites on the south-east of the area described.

2. 'The Geology of Southern Guernsey.' By Donald John Farquharson, M.Sc., F.G.S.

With the possible exception of some dykes of doubtful Palæozoic age, the whole of Guernsey consists of pre-Cambrian rocks—gneisses and schists in the south; unfossiliferous shales and grits at Pleinmont; and a series of intrusions in the north, which range from hornblende-gabbro through diorites and tonalites to granites with their accompanying dykes. These dykes not only pierce the last-named suite, but also the gneisses and grits of the south.

Prof. T. G. Bonney & the Rev. E. Hill were the first to study Guernsey geology on modern lines, and Mr. J. Parkinson has worked on the differentiation-suite of the north.

The succession appears to be as follows:—

? Palæozoic		Dykes (dolerite, quartz, lamprophyre, etc.).
Pre-Cambrian	C	Dykes (basic and acid). Granite (of Cobo). Differentiation-suite.
	B	Pleinmont Shale and Grit.
	A	Diorite-gneiss. Dykes (now metamorphosed). Granite-gneiss. Jerbourg Schists.

Group A consists of dynamically altered, foliated rocks, with a foliation ranging from north-west and south-east to north-east and south-west. The granite-gneisses are mostly porphyritic, and are characterized by abundant microcline. The dioritic gneisses, which verge on tonalites, occur at Divette and from Rocquaine to Torteval; the type characteristic of the last-named locality was first observed by the Rev. E. Hill near St. Andrew's brickfield, in 1884.

The Pleinmont Shale, first observed by Dr. G. H. Plymen, occurs more widely than was previously supposed, and is younger than the gneisses. It is followed by normal diorites and granites, which prevail in the north; but dykes of this set, mostly of dolerite, are very abundant on the southern coast. Some sill-like intrusions of a coarser dioritic rock occur in the gneiss of the eastern coast, and may be assigned to the differentiation-suite; this applies also to the picrite of Bon Repos, noted by Bonney & Hill. A spherulitic felsite occurs near Câtel, but its relations are obscure.